EFFECT OF SLURRY FLOW ON THE PRESSURE REQUIRED TO RESTART FLOW IN GELLED WAXY OIL PIPELINES AND CONNECTION TO RHEOLOGY

by

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STATEMENT OF THESIS APPROVAL

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ABSTRACT

As petroleum is becoming increasingly used worldwide, transportation of oil becomes more significant. Finding an effective method to transport petroleum would reduce costs. A pipeline is the most economical and efficient method for the transportation of large quantities of crude oil. However, since many pipelines are usually built under the sea, the ambient temperature is low. Paraffinic crude oils transported in pipelines normally form gels composed of wax crystals during flow shutdowns. These waxy gels may make it difficult to restart flow without breaking the pipe if pipeline flow ceases. A relationship between flow loop experiments and rheology measurements is studied and compared by using similar conditions. Gelled pipeline restart has two main cooling protocols: "slurry flow" and "hot flow." In hot flow, the waxy oil is cooled to the restart temperature under static, no flow conditions. In slurry flow, the oil is cooled during flow to the slurry temperature, and then cooled without flow to the restart temperature. Slurry flow restart became the focus of the author since it is expected to reduce wax deposition in pipelines. For the first and second version of the flow loop, the results showed how the slurry temperature greatly affects restart pressure after when the slurry temperature is below the wax appearance temperature (WAT). This study shows that the gel formed will be weaker when the slurry temperature is lower. This confirms previous research that concluded that varying the upstream pressure used in the range between 1 and 4 psig during the cooling period does not affect the strength of gel clearly.

Using a slurry flow method at a restart temperature of 5 °C requires less breaking pressure than hot flow restart. The strength of a gel formed by slurry flow is more than 10 times weaker than its hot flow counterpart. The breaking pressure obtained by converting the static yield stress measured from rheometer measurements under predicted the actual flow loop results. However, both the predicted yield stress and the measured yield stress showed similar trends, but differed by some constant value.

To my lovely family

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NOMENCLATURE

Notation

A	Surface Area of pipe
D	Diameter of Pipe
f_i^o	Pure Component Fugacity
G	Modulus or Mass Flow Rate of Gelled Oil Plug
G'	Storage Modulus
G''	Viscous Modulus
L, Z	Length of Pipe
P	Pressure
Δ P	Axial Pressure Drop
R	Radius of Pipe
S_i	Mole Fraction of Component i in Liquid Phase
t	Time
T_C	Coolant Temperature

T_d	Liquid-Deposit Interface Temperature
T_h	Mixture Temperature
Twi	Inside Pipe Wall Temperature
X_i	Mole Fraction of Component i in Solid Phase

Greek Letters

γ	Strain
γ_i^L	Activity Coefficients in Liquid Phase
γ_i^S	Activity Coefficients in Solid Phase
τ	Stress
τ_e	Elastic Yield Stress
τ_s	Static Yield Stress
τ_d	Dynamic Yield Stress
τ_w	Wall Shear Stress
θ_d	Fractional Deposit Layer Thermal Resistant

Acronyms

CCN	Critical Carbon Number
ICF	Incoming Fluid

OCF	Outgoing Fluid
WAT	Wax Appearance Temperature
WDT	Wax Disappearance Temperature
PPT	Pour Point Temperature

Definitions

Hot Flow Temperature:	The temperature when starts shutting in while temperature is above WAT
Restart Temperature:	The temperature when applies restart pressure to the gel
Slurry Temperature:	The temperature when stops flow while cooling below WAT

CHAPTER 1

IMPORTANCE OF FLOW ASSURANCE FOR WAXY CRUDE OIL TRANSPORT

Since crude oil is the most primary and important energy resource in the world, it is in high demanded. Oil supply has decreased exponentially with time since people use it in large amounts every day. Although crude oil prices have increased, the demand for petroleum has not dropped-off. Because the supply of lower percent wax crude oil is dwindling, highly percent wax crude oils are now being used [1]. The oil is transported via pipeline since it is efficient in cost of transportation and maintenance.

During flow shutdown, when ambient temperatures are low and below the Wax Appearance Temperature (WAT), paraffinic crude oils transported in pipelines may form waxy gels. Waxy crystals may deposit inside pipelines which causes flow to decrease [2], [3]. Normally, oil transportation industries use pressure to break these gels instead of increased heating to dissolve gels deposited inside the pipelines. Restart temperature affects how much wax could be deposited. In the case of crude oil produced off-shore, formation of solid deposits, which have a long carbon chain (carbon number >20), can easily become waxes [4]. D. Merino-Garcia and S. Correra claimed that almost all oil is transported as slurry, and only a small fraction of the waxes are deposited. This supports the idea of solids not participating in deposition. If they precipitate in bulk, they remain

in the bulk and are transported as slurry [4]. For subsea pipelines, in particular, it has become especially important to solve the wax build-up problem. Colder regions will be met with more serious wax precipitation as large scale oil production [5]. The timely removal of deposited wax is an important requirement to address since it causes a reduction in flow rate, and the removal prevents the eventual loss of a pipeline in the consequence that it becomes clogged [6].

In the experimental section of this study, two methods, which are hot flow and slurry flow, are performed and their restart pressures are compared with each other. For hot flow, there is no circulation of oil when the oil sample was cooled down. On the other hand, cold flow circulates oil inside pipelines as slurry. While the slurry is flowing, it creates a continuous shearing rate, so the slurry cannot form a proper gel structure and it will not adhere to the walls. This study reviews these patents and the experimental evidence that support the hypothesis of "Cold Flow" as shown in Figure 1.1 [4].

Figuring out the optimum pressure required to break the gelled waxy oil in the case of both hot flow and cold flow is the main objective of this research. At fixed ambient temperature, we study how the starting temperature affects the gelled restart pressure. The author is primarily interested in the case of slurry flow because it is useful and will be developed and used in the future. The author plans to use very wide temperature ranges in order to figure out how they affect the pipeline restart process.

Another goal of this research [2] is to find the relationship between flow loop experimental measurements and rheometric measurements. The conditions and methods used for the flow loop and rheometer are similar. The main difference is the units of measurement. While the rheometer uses a yield stress data, the flow loop utilizes

pressure. Many previous researchers have done both types of experiments by varying different conditions such as a cooling rate, cooling range, and fluid shear during cooling [7]. There are opposing ideas about the correlation between the rheometer and flow loop in the scientific community. Some researchers believe that the pressure drop applied from flow loop is underestimated [1]. Conversely, most researchers report that a rheometric yield stress data overestimates the pressure needed to break a gel in a flow loop pipeline test [2, 8, 9]. For this reason, the author is interested in finding out the relationship between flow loop results and rheometric measurements.

1.1 Deposition of wax and wall effects

Deposition of wax is the main problem occurring in transportation of oil which is a complex mixture containing heavy wax such as naphthenes, aromatics, paraffins, asphaltenes, resins, etc. like crude oil [10]. In a subsea environment, the ambient temperature is below the wax appearance temperature of the gel, it causes wax to precipitate out of the fluid and deposit on the pipe wall. It costs a lot of money and time to maintain system.

Many theories have been proposed to demonstrate gel deposition method on a cold surface such as diffusion of Brownian movement and molecular, gravity settling and shear dispersion [10, 11]. Singh et al. [12] explained that "An external convective mass flux of wax molecule from the bulk oil flow toward the cold wall and internal diffusive flux within the gel layer are responsible for the growth and aging of gel deposition."

Singh et al. [12, 13] developed a deposition model that can check the buildup of wax and rate of aging, which affects the molecular diffusion of paraffin from fluid to the layer on the pipe wall. The solid fraction increases due to the precipitation of paraffin

components that deposit on the wall**.** To measure the wax deposition in the pipe surface, Venkatesan et al. used oscillatory rheometric measurement instead of using a flow loop [14].

The slip condition could be very significant for flow loop and rheometer results. For the flow loop, since the results mean nothing if the waxy gelled oil slips from the pipe wall during cooling in the flow loop. Moreover, Phillip stated that [7] "there would be no flow deformation if the shrinkage movement relative to the wall is from frictional slip, it would be no meaning of actuating pressure transducer." However, previous researchers have found that the geometry of the measurement system is the main factor for wall effects. Wax composition and surface roughness are also significant. To sum up, they concluded that there will be no slipping for gelled waxy oil which can make a strong wax deposit on the wall in a pipeline [7].

An increase in the temperature of the solution of waxy oil and flow rate (Reynold number increase) causes decreasing mass deposition. Similarly, increasing the cooling temperature also make lower mass deposition [15].

1.2 Removing wax method

Many methods of wax deposition prevention have been explored for a half century, such as pigging, adding chemical additives, line heating, using insulation, electric and magnetic process and etc. [16, 17]. Only pigging, chemical adding, and heating process are the most common used in reality. However, these methods can be costly and messy, especially in when the pipeline is set up in the extreme position, so it makes a difficult situation to get rid of the wax deposition and other issues. "Cold flow" is the new method to solve wax deposition in the pipeline. For a decade, researchers have

been interested to study how "cold flow" works because it is a normal and inexpensive process. The concept of "cold flow" is minimizing wax deposition by reducing the heat flux inside the pipeline reported by Jemmett et al [3].

1.2.1 Pigging

The most popular technique used to remove wax deposition inside the pipe wall is pigging. This method works by scraping waxy deposits and build-ups inside the pipe. Pigging is usually required 3-4 times a month and is essential for the maintenance of many pipelines. However, the risk of pigging should be considered because pigs become stuck very often and can damage the pipeline. The cause of pigging problems is related to pigging frequency, velocity adjustment and pig type. Moreover, multiple diameter sizes can cause pigging failure.

Measurement of a pressure drop can detect whether there is a significant buildup of waxy gelled oil in the pipeline. The pressure drop along a pipeline is proportional to the square of the diameter, so this means that a pressure difference between two axial positions gives evidence of the presence of a wax deposition in the line. To sum up, even though pigging is very common and used widely, a lot of risk is involved, in addition to it being a cumbersome and expensive process [18].

1.2.2 Additional chemical

The concept of adding additional chemicals is to limit or minimize wax solidification and crystal growth. Chemical additives inhibit and delay wax aggregate formation which blocks the growth of heavier wax deposits in the pipeline. Polymers

which have a long alkyl side chains, such as acrylate polymers, are known to reduce the rate of wax formation [19].

1.2.3 Cold flow

Heat flux elimination is a key factor in designing a cold flow system, since the idea is that waxes will not deposit to the wall surface if the temperature difference is zero. When the temperature of the oil and the ambient temperature outside the pipe is the same, there is no driving force to change phases and no deposition occurs in the system [18]. No doubt that the primary wax appearance temperature of waxy crude oil is above ambient conditions, so the solid-liquid slurry transported state is required with solids being precipitated wax crystals [4, 20]. To transport the slurry, a higher powered pump is required, since the viscosity of the fluid rises because of wax crystals in the slurry. Moreover, Venkatesan et al. observed that the gel formed in the rheometer from "cold flow" is weaker than a gel formed from hot flow. This knowledge is very useful for industrial application in the future [21].

1.3 Wax appearance temperature (WAT)

Wax Appearance temperature (WAT) is the first temperature that wax precipitates out of solution. It does not seem to depend on shear history or kinetics, WAT is a physical property that depends on the oil used and its wax content. However, Jemmett et al. [3] observed that the WAT and wax disappearance temperature (WDT) are not fixed in value because of kinetic limitations. They demonstrated that WAT and WDT could be the same when heating or cooling at extremely low rates. Otherwise, the WDT is higher than WAT because it could take more time and energy to melt the precipitated solid back to the solution.

1.4 Force balance in flow loop and correlation with rheometer

When cooled below their gelation temperatures, waxy crude oils of course vary greatly in composition and in the strength of the gels that they form. Rheological properties are used to predict the minimum restart pressure required to break waxy gels in pipelines. The yield stress is defined as the maximum shear stress that the gel can withstand without fracture or flow [3]. The force balance in the pipeline is shown in Figure 1.2. The wall shear stress exerted on the gel at a given axial position z is related to the axial pressure gradient (dP/dz). The resulting equation is given by Eq. 1.

The axial pressure shows a linear profile. Furthermore, the whole length of the gel could break simultaneously at a minimum value of the applied pressure given by Eq. 2 [3].

$$\tau_S = 0.5\, R \left(-\frac{dP}{dZ}\right) = G\gamma \qquad (1)$$

$$\Delta P_{min} = 2\frac{L\tau_S}{R} \qquad (2)$$

However, Magda et al. [2] reported that having voids in the oil in the gelation process answers why the pressure profile cannot be linear and why gel breaking occurs at less required pressure than predicted by Eq. 2. Previous researchers had similar conclusions in that the yielding process of the waxy gelled oil is time dependent [2, 22-26]. Moreover, scientists also observed that gel temperature and shear history affect the development of gel structure and strength of the gel [7, 10, 26-29].

1.5 Gelation temperature and thermodynamics view

Figure 1.3 shows how to measure the gelation temperature of 7 wt % wax dissolve in superla mineral oil. The value of G' becomes greater than G''at 22-23 °C, this condition is the gelation temperature, the temperature that the oil becomes a gel [2]. Modification thermodynamic consideration, presented by Pedersen [30] has been used in this study to predict WAT and the amount of wax formed at a given temperature.

Eq. 3 works for the vapor–liquid–solid equilibrium for phase equilibrium prediction of oil mixtures to determine a wax build up.

$$f_i^S = X_i^S \phi_i^{oL} p \exp[(-\Delta H_i^f)/RT\,(1 - T/T_i^f)] \qquad (3)$$

The equilibrium between paraffin (component *i*) in mixture and solid can be predicted by equating the fugacity in the case of the solid-liquid phase as shown in Eq. 4

$$X_i \gamma_i^L f_i^{oL} = s_i \gamma_i^S f_i^{oS} \qquad (4)$$

where x_i and s_i are the liquid and solid mole fractions of component *i* correspondingly, γ_i^L and γ_i^S are the liquid and solid activity coefficients, respectively, and f_i^o is the fugacity of pure component [10].

1.6 Start-up type in flow loop

There are three possibilities for starting the flow for homogenous tests such as start-up without delay, start-up with delay and unsuccessful start-up, and one more for heterogeneous. It all depends on the wall shear stress (τ_W), which is applied to the pipeline. The primary gel strength, which is defined by its gel properties such as elastic-

limit yield stress (τ_e) and static yield stress (τ_s), results in type of restart as stated by Chang et al. [31].

1.6.1 Start-up without delay

A fixed applied pressure is imposed as the wall shear stress (τ_w) exceeds the static yield stress of the waxy gelled oil (τ_s). ($\tau_w > \tau_s \; when \; t = 0$).

1.6.2 Start-up with delay

If a fixed applied pressure that is imposed as the wall shear stress (τ_w) is in between the elastic-limit yield stress (τ_e) and the static yield stress(τ_s). ($\tau_e < \tau_w < \tau_s$).

1.6.3 Unsuccessful start-up

It occurs when applied pressure as the wall shear stress (τ_w) is lower than the elastic-limit yield stress (τ_e). ($\tau_w < \tau_e$).

1.6.4 Heterogeneous start-up

The pattern of heterogeneous restart would be dissimilar with the homogenous restart since position and type of breaking are different. Heterogeneous restart is a cohesive failure when the waxy gelled oil is broken within their structure itself. In contrast, homogenous restart is adhesive failure when the gelled oil is restarted at the gel-wall [32]. Moreover, Lee et al. [33] discovered (by using rheometric measurement) that the failure stress and failure type are dependent upon the cooling rate.

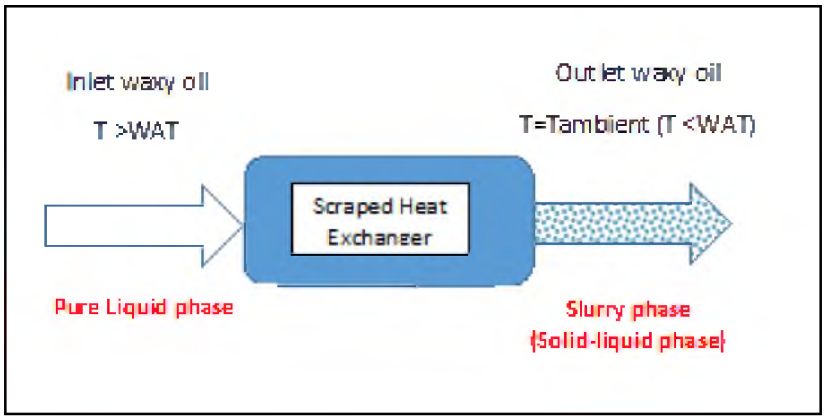

Figure 1.1. Cold flow idea. This figure is adapted from (Merino-Garcia et al., 2008, Figure 1) [4]

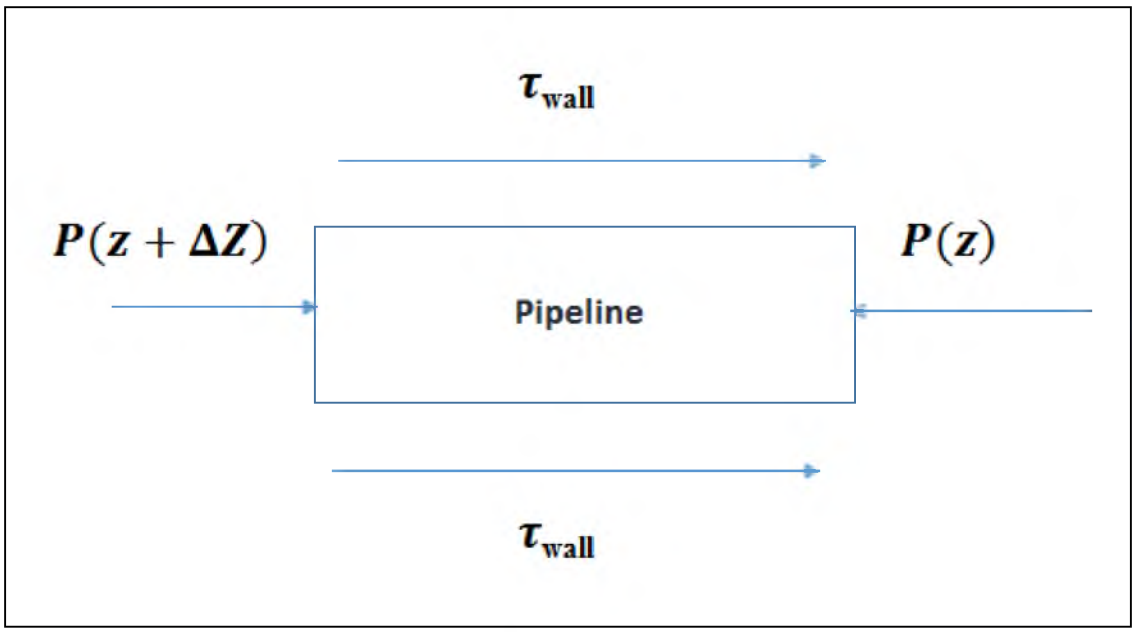

Figure 1.2. Force balance in pipeline. This figure is adapted from (El-Gendy et al., 2011, Figure 1) [3].

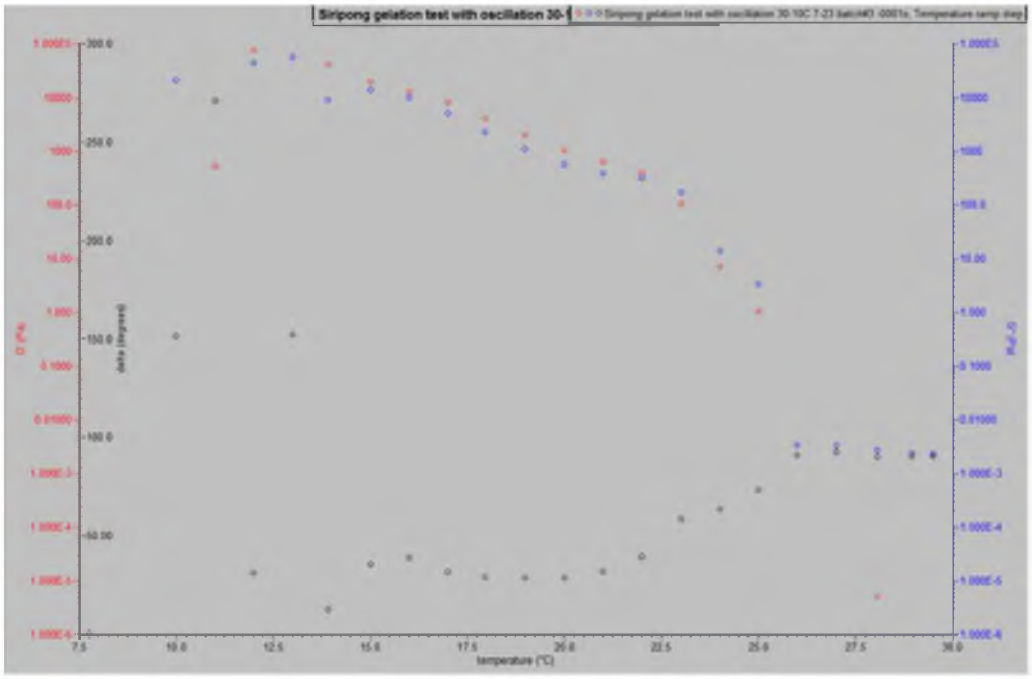

Figure 1.3. Gelation temperature of 7% model waxy oil. The gel point is defined as the temperature where the elastic modulus surpasses the viscous modulus, which is approximately 22-23 °C.

CHAPTER 2

FLOW ASSURANCE – A LITERATURE REVIEW

2.1 Introduction

Many researchers have been interested in studying flow assurance, especially methods related to the transportation of petroleum like crude oil because the pipeline is placed under the sea and the ambient temperature is lower than the wax appearance temperature (WAT), wax can deposit inside the surface of the pipe. First, thermal differences between the cold outside of the pipe and hot oil inside the pipe can cause a layer of wax to form on the inside of the pipe, then additional wax will continue to deposit after time has passed. The author would like to review significant flow assurance literature to develop an effective and cost efficient method for the transportation of petroleum via pipeline.

2.2 Literature

2.2.1 Chang, Boger and Nguyen (1998)

Chang, Boger and Nguyen [34] studied yielding process using a controlled stress rheometer which they concluded to be the best tool to determine a true yield stress. They observed that the waxy crude oil yielding is a complicated process which includes three steps: elastic, creep and fracture response.

The oils they used were DH19 waxy crude oil and BO to repeat the experiment. The Carri-Med CSL 100 rheometer with cone and plate was used to measure all yielding processes. They stated that the use of a cone and plate gives a lot of advantages overusing a flat plate because shear rate and shear stress are uniform to the materials when the cone angle is small.

Controlled stress tests, creep-recovery tests, and oscillatory tests were three tests they used. They observe that the dynamics yield stress (τ_d) can be identified from static yield stress (τ_s) which was received from direct measurement. They defined only two of the three types of yield stress. The elastic limit yield stress (τ_e) occurs when creep starts and static yield stress occurs when gel starts to fracture. However, they did not state the definition of dynamic yield stress. The static yield stress measured from the rheometer might not work well when designing pipelines because static yield stress is time dependent and the stress loading rate might also affect the correlation between them.

They concluded that the transition between partial and full recovery of the gel can be defined as elastic limit yield stress and the transition between partial recovery and fracture of the gel is the static yield stress. In the other word, the elastic limit yield stress was between 4 and 8 Pa and the static yield stress was between 16 and 20 Pa in their case.

They concluded that static yield stress can be measured by all tests, but the elastic limit yield stress can be produced from creep recovery and oscillatory tests. The results received from all three techniques are in good agreement.

2.2.2 Singh, Youyen and Fogler (2001)

Singh, Youyen and Fogler [35] studied the critical number in the aging of a wax-oil gel. They observed that the critical number is defined diffusion direction of carbon in the solution.

They concluded that when hydrocarbon has a higher carbon number than critical carbon number (CCN), it would diffuse into the deposit the layer which attaches to the wall surface. In contrast, it would diffuse out of the layer if the carbon number is less than CCN. The results demonstrated that changing of carbon in the layer was a negative 28 or less carbon number, and a delta of the carbon number in the gel deposition is positive for a carbon number higher than 28. It is obvious that the critical carbon number (CCN) of material was 28.

Singh, Youyen and Fogler [35] summarized 5 steps of the wax deposition process as followed:

1. Gel occurs as a layer on the cold surface.
2. Wax diffuses from bulk fluid to the layer.
3. Hydrocarbon, which has a carbon number higher than CCN, will internally diffuse to the cold layer.
4. Molecules precipitate to inside the layer.
5. Hydrocarbon, which has a carbon number lower than CCN, will counter diffuse to the bulk.

2.2.3 Davidson, Nguyen, Chang and Rønningsen (2004)

Davidson, Nguyen, Chang and Rønningsen [1] studied a model used to predict the restart of a pipeline with compressible gelled waxy crude oil. What they observed was

that gelled waxy crude oil has an effect on fluid-oil interphase mobility, oil flow rate, and clearing time to remove waxy gelled oil.

They created a model which used another fluid under constant pressure to pump fluid in order to remove gelled waxy oil deposited in the pipeline. The incoming fluid exhibited Bingham plastic behavior. The incoming fluid (ICF) might be water or oil that has similar properties with the waxy gelled oil used to get rid of gelled oil that becomes outgoing fluid (OGF). They applied constant pressure to ICF to push OGF, and the gel would be broken after imposing enough pressure to exceed the pipe wall shear stress.

They predicted the applied pressure drop as $\Delta P > 4\tau_S L/D$, where τ is the static yield stress of oil. Numerical models were used to demonstrate the results. They selected dimensionless parameters when presenting the results. The results showed that the clearance time was reduced exponentially when the applied pressure was increased. The effects of thixotropic behavior, compressibility, and yield stress were presented by their model.

2.2.4 Davidson, Nguyen and Rønningsen (2007)

Davidson, Nguyen, Chang and Rønningsen [36] continued to use their numerical model that had been developed to discover gelled waxy oil restart conditions. This time they focused on a restart model for a multiplug gelled waxy oil pipeline and checked the effect of shrinkage when shutting down the system before restart. The experiment was prepared by filling the pipeline with plugs of gelled oil separated by gas.

The overall idea and method used are very similar to work they had done before [1]. They applied pressure from another fluid that had the same properties to displace the waxy oil inside the pipeline. The main purpose was using high enough pressure to create

shear stress to exceed the static yield stress. After applying a constant pressure drop exceeding the shear stress at the wall in the first plug, the gel structure started to break down. At ($t \geq t_0$), both incoming fluid (ICF) and the first outgoing fluid (OGF) plug moved at the same flow rate after the yield front had gone through the gelled oil in the single plug. In contrast, for multiple plug flow, the mass flow rate would be dissimilar because of a volume change in the gas zone when flow carries on. Eq. 5 shows the relationship between both mass flow rates since the velocity is a difference between the ending of plug 1 and the beginning of plug 2. G_1 and G_2 represented the mass flow rate of gelled oil of plug 1 and 2, respectively.

$$G_1 = \rho_1 \left(\frac{G_2}{\rho_2} - A \frac{dL_g}{dt} \right) \quad (5)$$

The results they observed were that increasing restart pressure deceased the clearance time needed to remove the gelled oil. They compared the result in 2 cases between multiplug (plug1: gas: plug2), by percentage length distribution (50:20:30), and single plug at the same 80 % liquid hold up and checked the interface position; multiplug had a higher interface position compared to the single plug.

Another thing they discovered was that clearance time decreased when increasing the length of the gas section and varying the initial pressure in the range of 1 to 5 bar did not affect the results.

2.2.5 Lee et al. (2008)

Lee et al. [33] studied waxy oil gel breaking mechanisms between cohesive and adhesive failure. They used a model flow loop apparatus made by a stainless steel tube which was 0.77 cm in diameter and 3.77 in length, and used a water bath as a cooling

system. The oil used was a model wax-oil mixture which contained 15% of food grade paraffin, 33% of kerosene, and 52% of mineral oil.

The results showed that no liquid penetration occurred since the inlet pressure maintained a constant value. At a restart temperature of 15.1 °C, gel broke at approximately 170 kPa which was weaker than a restart temperature of 12.7 °C. Upstream pressure was not applied in their pipeline system. Volume reduction occurs during a cooling process. It requires higher pressure to break a compressed gel at lower temperatures. At a restart temperature of 12.7 °C, the volume reduction was highest at 1.7%.

There are two types of gel structure breakdown. One is a cohesive failure where the breakdown is in the gel structure itself. The other is adhesive failure, which occurs when the gel breaks at the interface of pipe and gel. When dealing with adhesive failure, increasing the cooling rate results in a higher yield stress. On the other hand, when dealing with cohesive failure, increasing the cooling rate results in a lower yield stress. Venkatesan [14] also shows a relationship between type of gel structure breakdown and cooling rate.

The crystal size of the wax deposit was larger and the crystals had a sheet-like shape at the lower cooling rate (3.5 °C/min). In contrast, the crystal structure was smaller and the crystals had a needle-like shape at a higher cooling rate (20 °C/min).

2.2.6 Bidmus and Mehrotra (2009)

Bidmus and Mehrotra [20] studied on solid deposition of solvent mixtures under cold flow conditions in the flow loop using heat transfer. First, they used the definition of "cold flow" from Garcia and Correra who state that "Cold flow refers to the pipeline flow

of a "waxy" crude oil at a temperature, which is below its wax appearance temperature (WAT) and above its pour point temperature (PPT), whereby precipitated wax crystals remain suspended in the flowing crude oil" [4].

They used 3% and 6% wax dissolved in Norpar 13. Their main idea about cold flow and hot flow was that the temperature of cold flow is between wax appearance temperature (WAT) and pour point temperature (PPT) while the temperature of hot flow is higher than WAT.

Cold flow (wax crystals precipitated in the crude oil) could be a new approach to prevent or reduce wax deposition in the pipeline during flow of the waxy crude oil. The idea of cold flow is to reduce a thermal difference between hot oil and the cool ambient environment by flowing formed slurry at a temperature near the ambient temperature. They used a bench-scale flow loop apparatus to measure the wax deposition for hot flow and cold flow using heat transfer between mixture and coolant to make a wax deposition.

The ratio of the the deposit layer of thermal resistance to combined thermal resistance (θ_d) was stated by Bidmus and Mehrotra [37] as shown in Eq. 6.

$$\theta_d = \frac{R_d}{R_h + R_d + R_m + R_c} = \frac{T_d - T_{wi}}{T_h - T_c} \qquad (6)$$

T_d is liquid-deposit interface temperature, T_{wi} is inside pipe wall temperature, T_h is mixture temperature and T_c is coolant temperature. This equation became significant because when the difference between mixture temperature and coolant temperature is zero (θ_d is infinity), no deposition occurs inside the pipeline wall. In other words, there is no thermal driving force in the system. The deposit of mass per unit area

increased when θ_d increased. Again, when θ_d equals zero, there will be no mass deposition.

They showed the effect of change in mixture temperature of 3% and 6% wax dissolved in the solvent at a flow rate of 10 L per minute. They observed that the temperature profile of T_h and T_d was approximately parallel when the temperature was below WAT. Deposit of mass increases with a decrease in mixture temperature for the hot flow case. In contrast, the deposit of mass increases with an increasing mixture temperature for cold flow. In other words, the amount of deposition is greatest when the mixture temperature is closest to WAT. One thing that they observed was that the Reynolds number did not affect the deposition of mass, this was contrary to previous research. The mass deposition decreases with Re increases.

2.3 Summary of main literature review and gaps in published research

Three main literature reviews illustrate the main points about rheology and cold flow conditions (slurry flow), which are related to the author's thesis. Previous researchers have performed several rheological tests such as controlled stress tests, creep-recovery tests, and oscillatory tests used to measure gel behavior. They demonstrate how three yield stresses such as elastic limit yield stress, static yield stress, and dynamic yield stress become important in flow assurance.

Previous researchers have explored one of the best ways to reduce or prevent the deposition of wax inside pipelines surrounded by cold ambient temperatures called cold flow. Flowing the waxy crude oil at a temperature between WAT and PPT can prevent or reduce the deposition of wax. Also, the strength of the gel formed is not strong compared to the hot flow case. There is no deposition if the temperature difference between the

mixture of wax-solvent and the environment is zero. The amount of wax precipitate is greatest when the mixture temperature is closest to WAT. The mass deposition decreases when the speed of flow is increased or the Reynolds number is increased. However, it is still necessary to explore this field more. Previous researchers have not studied slurry tests with rheometric measurement and the relationship between the flow loop and rheometer under slurry flow conditions. A question is whether a constant upstream pressure applied to the system while statically cooling will affect the results.

2.4 Novelty of this thesis

Previous researchers have explored a lot of details related to flow assurance. However, there are still gaps in published research that need to be filled. For this reason, the author has felt interested in partaking in flow assurance research. The novelties of this thesis are as follows: (1) Figuring out the restart pressure required to break the gel for the flow loop with a constant upstream pressure applied under slurry flow conditions, (2) figuring out the yield stress required to break the gel for the rheometer after cooling with a constant low shearing rate applied under slurry flow conditions, and (3) finding the correlation between the rheometer and flow loop under slurry flow conditions. The last novelty is the most important because if the author can find out the relationship between the flow loop and the rheometer, flow loops will not have to be used and a rheometer can be used to measure gel properties instead. This would save in materials, time and costs required to predict the strength of a gel and how much pressure would be required in order to break gel deposits inside field pipelines.

CHAPTER 3

EXPERIMENTAL SETUP AND PROCEDURES

3.1 Materials

Model waxy crude oils are needed for the experiment to circulate in the flow loop apparatus. The model waxy oil is prepared by adding 7 percent of wax (food grade) to Superla mineral oil (specific gravity 0.85, viscosity 20 mPa s at 25°C). The model waxy oil is shown in Figure 3.1. Any volatile components are not considered in order to avoid an evaporation problem that might occur. The carbon number distribution of wax (food grade) dissolved in superla mineral oil is shown in Figure 3.2. It is measured with high temperature gas chromatography (HP 5890) [2].

3.2 WAT measurement

Rheometer is generally known as viscosity inspection. However, it can apply to use in other kinds of tests such as gelation, creep, oscillation as well as WAT test. Figure 3.3 represents WAT from an Arrhenius plot. Logarithm of viscosity was plotted with the inverse of temperature. When the value of viscosity changes rapidly, it means that phase of a sample changes. The figure shows that WAT of waxy oil is 25-26 °C. On the other hand, water bath is used to control temperature. It is highly recommended to use a temperature controller. The oil contained in the glassware was cooled in the water bath.

WAT was measured between 27 and 28 °C. In the case of flow loop, by manually observing, WAT was 26.5-27.2 °C. The author defined WAT of 27 °C as measured by water bath because it measured under static conditions without any shear imposed.

3.3 Flow loop

The Utah Petroleum Research Center laboratory flow loop is the main apparatus using thermocouple, pressure transducers (omega PX 309) to measure the temperature and pressure of oil samples, respectively. Because a thermocouple and pressure transducer can detect the signal in a voltage unit, signal adapter and lab view software are needed to get the useful data.

3.3.1 Flow loop the first version

The first version of flow loop was developed to figure out the optimum pressure required to break waxy gelled oil deposited in the pipeline. It had one loop and one reservoir, one pump, one pressurized reservoir, two main valves, and a cooling system. Figure 3.4 shows a diagram of the first version of the flow loop

3.3.2 The second version of flow loop

To get rid of deposition while making a slurry flow, and to get more precise results, the second version of the flow loop was desired. The second version of the flow loop has two loops which are the experimental loop and conditioning loop. Figure 3.5 and Figure 3.6 shows the picture and diagram of the second version of the flow loop, respectively. The dimension of the flow loop is shown in Figure 3.7. The elements of the loop are shown by various figures, such as the pressurized reservoir and nitrogen gas cylinder (Figure 3.8), the cooling machine and scraped heat exchanger (Figure 3.9),

conditioning loop pump and the experimental loop (Figure 3.10), and pressure transducers (Figure 3.11). Slurry restart testing is the main purpose of this research. Due to this, the author needed to use the second version of the flow loop which has a scraped heat exchanger used to remove wax deposition on the pipe wall during slurry flow, instead of the first version. Table 3.1 shows a component list of flow loop second version.

3.4 Rheometer

An AR 500 rheometer is used to find the static yield stress, gelation temperature and modulus. Figure 3.12 and Figure 3.13 show the AR 500 rheometer and cone and plate, respectively. Since the AR 500 rheometer had been used for a long time, it could not reach the steady temperature at 5 °C or below, so Discovery HR (see Figure 3.14), a brand new rheometer, has been used to measure a yield stress at a fixed temperature of 5 °C. The correlation between flow loop and rheometer is the main point that the author is interested in.

3.5 Experimental methods

3.5.1 Flow loop

3.5.1.1 Hot flow restart method

First, open the upstream and downstream valves from the test section and conditioning loop to be ready to run the experiment. Then heat 7% of the model oil up to 50 °C and circulate the model oil by using the experimental and conditioning loop pump. After reaching 50 °C, close the downstream valve and open the pressurization valve by letting oil flow up 2 inches in the reservoir; then close the pump and upstream valve. In the cooling period, cool down the oil sample by using ethylene glycol flow and exchange

heat outside the model pipe at a rate of 0.3 °C per minutes and impose a pressure of 4 psig to the system. Wait until the gel reaches a steady state temperature (restart temperature), and finally check the restart pressure.

3.5.1.2 Slurry flow restart method

The procedure starts by opening the upstream and downstream valves of the conditioning loop to prepare to run the experiment. Make sure to close the upstream valve of the testing loop before turning on the conditioning loop pump. Then heat the oil up to 50 °C while it is circulating through the loop. After the temperature reaches 50 °C, then make the slurry oil by cooling down the oil sample while circulating the oil to the desired shutdown temperature. Set the experimental section coolant temperature to the desired shutdown temperature. After the slurry oil reaches the desired temperature, open the upstream valve connected to the test section. The next steps are closing the conditioning loop pump, opening the test section pump, closing the downstream valve. Open the pressurization valve and let 2 inches of oil flow up in the reservoir; then close the pump and upstream valve. Start cooling the oil to the desired restart temperature and wait until the gel is at a steady state for one hour. Finally, check restart pressure.

3.5.2 Rheometer

The author is interested in two types of testing for the rheometer, which are hot flow and slurry flow testing. Applying a shear stress while cooling in the rheometer is analogous to slurry flow in the flow loop. Similarly, static cooling from the desired shutdown temperature to restart temperature is analogous to hot flow restart. The author shows the procedure for doing both tests as follows

3.5.2.1 Without shearing (static restart procedure)

1. Clean the peltier plate and 2 °C cone with acetone
2. Put superla model oil containing 7% wax into a 50 °C oven, and wait 30 minutes
3. Start rheometer software (Rheology Advantage Instrument Control AR)
4. Calibrate instrument inertia
5. Connect the cone to the rheometer
6. Calibrate geometry inertia and bearing friction
7. Set gap compensation at 0.5 μm
8. Lower the gap down to 48 μm and heat the peltier plate to 40 °C
9. After the desired temperature is reached, wait 10 minutes for equilibrium. Raise the gap to around 15,000 μm, and put the oil sample on the peltier plate
10. Click zero gap and wait 10 minutes for equilibrium at 40 °C
11. Select oscillation test and apply a frequency of 0.02 Hz and a shear stress of 0.8 Pa
12. Run the experiments
13. After the gel reaches the restart temperature, run a creep test
14. Impose a shear stress to a gel. If the gel does not break, increase the shear stress by suitable increment, and run another creep test
15. Record and save data

3.5.2.2 With shearing (slurry restart procedure)

1. Clean the peltier plate and 2 °C cone with acetone
2. Put superla model oil containing 7% wax into an oven, and wait 30 minutes at 50 °C
3. Start rheometer software (Rheology Advantage Instrument Control AR)
4. Calibrate instrument inertia
5. Connect the cone to the rheometer
6. Calibrate geometry inertia and bearing friction
7. Set gap compensation at 0.5 μm
8. Lower the gap down to 48 μm and heat the peltier plate to 40 °C
9. After the desired temperature is reached, wait 10 minutes for equilibrium. Raise the gap to around 15,000 μm, and put the oil sample on the peltier plate
10. Click zero gap and wait 10 minutes for equilibrium at 40 °C
11. Use flow method in the rheometer software, and cool the sample down to desired slurry temperature while flowing with a rate of 0.3 °C/min
12. When the temperature reaches desired slurry temperature, select oscillation test and apply a frequency of 0.02 Hz and a shear stress of 0.8 Pa. Set the final restart temperature
13. Run the experiments
14. After gel reaches the restart temperature, run a creep test
15. Impose a shear stress to a gel. If the gel does not break, increase the shear stress by suitable increment, and run another creep test
16. Record and save data

3.6 Flow loop experimental design

3.6.1 First version of flow loop

3.6.1.1 Investigating how restart temperature for hot flow restart affects the restart pressure to break waxy gels

1. Open the upstream and downstream valves
2. Start the temperature controller and heat the 7% waxy oil up to 50 °C
3. Circulate the oil in the flow loop via pump and turn on the mixing blade
4. After the temperature of the oil reaches 50 °C, close the downstream valve, and open the pressurization valve. Let oil flow up 2 inches in the reservoir
5. Close the pump and upstream valve
6. Impose a pressure of 4 psig to the system
7. Cool down the oil by a temperature controller to the restart temperature at a rate of 0.3 °C per minute
8. Click record in the LabVIEW software
9. After the temperature of the gel reaches the desired temperature, wait 1 hour for equilibrium
10. Open the downstream valve and allow 10 minutes for equilibrium
11. Impose a pressure of 10 psig. If the gel does not break within 2 minutes, increase the pressure in increments of 5 psig
12. Monitor the downstream pressure. When the pressure suddenly raises and a sound is heard, this means the gel is broken
13. Save and stop recording

3.6.1.2 Figuring out if upstream pressure affects the strength of waxy gels

Basically, this procedure is done in the same fashion as the previous procedure except the upstream pressure is varied. Vary the upstream pressure between three conditions which are 1 psig, 4 psig, and 10 psig. Keep the restart temperature constant at 15 °C, and finally check the restart pressure.

3.6.1.3 Using slurry method to investigate restart pressure

1. Open the upstream and downstream valves to be ready to run the experiment
2. Start the temperature controller and heat the 7% waxy oil up to 50 °C
3. Circulate the oil in the flow loop via the pump and open the mixing machine
4. After the temperature of the oil reaches 50 °C, cool down the oil to slurry desired temperature (20 °C), and wait until the slurry temperature reaches the desired temperature
5. Close the downstream valve, and open the pressurization valve by letting oil flow up 2 inches in the reservoir
6. Close the pump and upstream valve and impose a pressure of 4 psig to the system
7. Cool down the oil by cooling machine to a restart temperature with rate 0.3 °C per minute
8. Click record in the LabVIEW software
9. After the temperature of the gel reaches the desired restart temperature, wait for equilibrium (about an hour)
10. Open the downstream valve and allow 10 minutes for equilibrium
11. Impose a pressure of 10 psig. If the gel does not break within 2 minutes, increase the pressure by increments of 5 psig

12. Listen for the gel breaking sound, then check the breaking pressure and click record again

3.6.2 Second version of flow loop

3.6.2.1 Investigating how restart temperature for hot flow restart affects restart pressure to break waxy gels.

1. Open the upstream and downstream valve for experimental loop and conditioning loop
2. Open the heating machine and heat the 7% waxy oil up to 50 °C
3. Circulate the oil in the flow loop via pump and open the mixing machine
4. After the temperature of the oil reaches 50 °C, cool the oil down to 40 °C
5. After the temperature of the oil reaches 40 °C, close the downstream valve, and open the pressurization valve. Let oil flow up 2 inches in the reservoir
6. Close pump and upstream valve
7. Impose a pressure of 4 psig to the system
8. Cool down the oil by cooling machine to a restart temperature with rate 0.3 °C per minute
9. Start recording in the LabVIEW software
10. After the temperature of the gel reaches the desired temperature, wait for equilibrium in about an hour
11. Open the downstream valve and allow 10 minutes for equilibrium
12. Impose a pressure of 4 psig. If the gel does not break within 2 minutes, increase the pressure by increments of 4 psig

13. Monitor the downstream pressure. When the pressure suddenly raises and a sound is heard, this means the gel is broken
14. Save and stop recording

3.6.2.2 Using slurry method to investigate the restart pressure

1. Open the upstream and downstream valve for the conditioning loop, and close the upstream valve for the experimental loop
2. Open the conditioning temperature controller and heat the 7% waxy oil up to 50 °C
3. Circulate the oil in the flow loop by conditioning loop pump and open the mixing machine, and open scraped heat exchanger and fan motor with full power
4. After the temperature of the oil reaches 50 °C, cool the oil down to 40 °C, and wait for equilibrium
5. Cool the waxy oil to the desired starting slurry temperature
6. After temperature is constant at desired slurry temperature, open the upstream valve for the test section and open the experimental pump
7. Turn off the conditioning loop pump, scraped heat exchanger, and fan motor
8. Open the pressurization valve by letting oil flow up 2 inches in the reservoir
9. Turn off the experimental section pump and the upstream valve connected to the experimental test section
10. Impose a pressure of 4 psig to the system
11. Cool down the oil by the temperature controller to a restart temperature with a rate of 0.3 °C per minute
12. Click record in the LabVIEW software

13. After the temperature of the gel reaches the desired temperature, wait an hour for equilibrium
14. Open the downstream valve and allow 10 minutes for equilibrium
15. Impose a pressure of 4 psig. If the gel does not break within 2 minutes, increase the pressure by increments of 2 psig
16. Monitor the downstream pressure. When the pressure suddenly raises and a sound is heard, this means the gel is broken
17. Save and stop recording

Figure 3.1. Superla waxy oil.

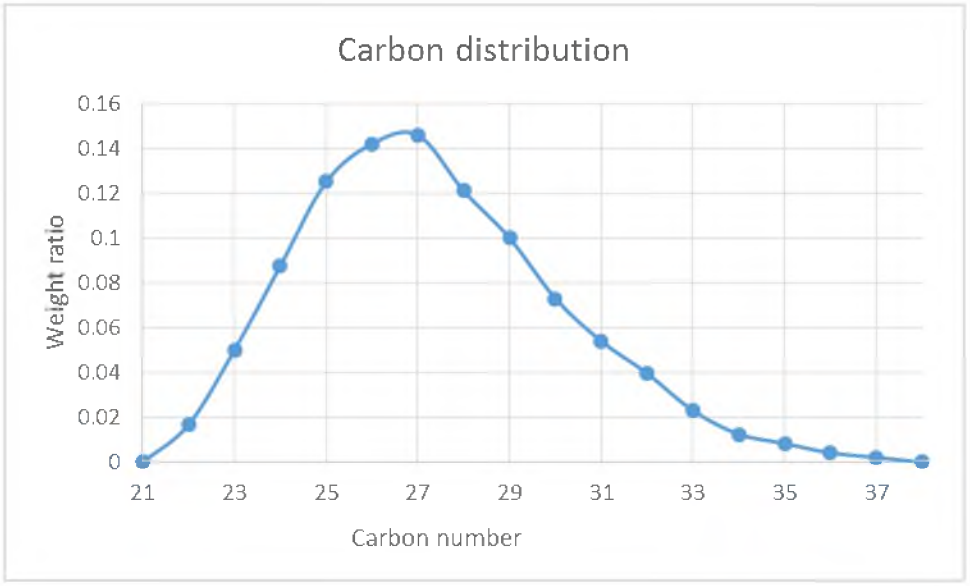

Figure 3.2. Carbon number distribution of waxy oil. This figure is adapted from (Magda et al., 2009, Figure 1) [2]**.**

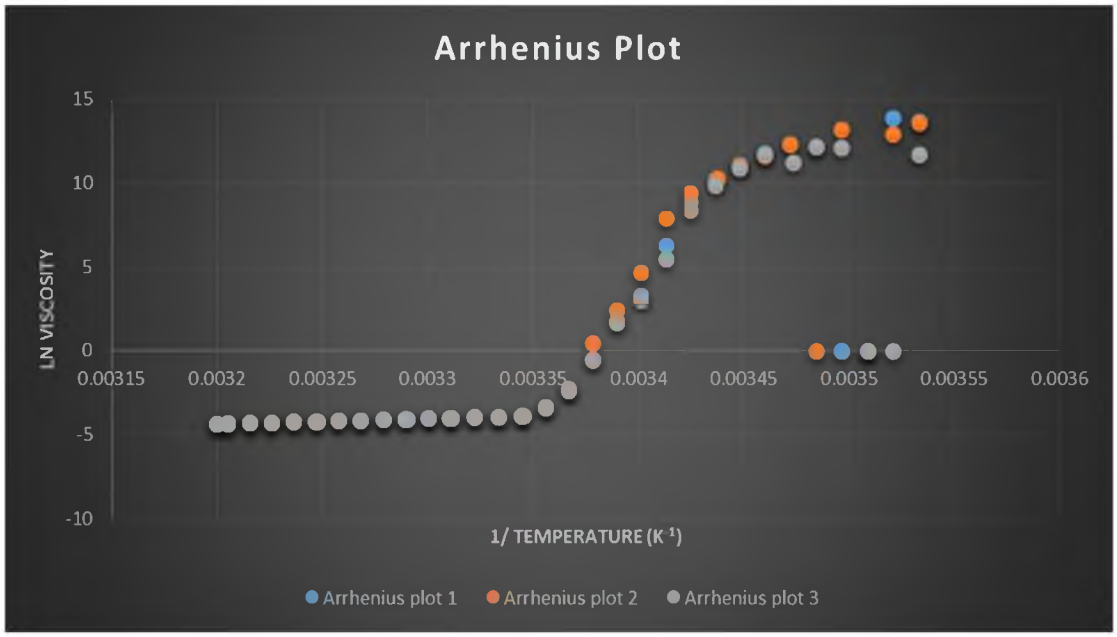

Figure 3.3. Arrhenius plot represents wax appearance temperature.

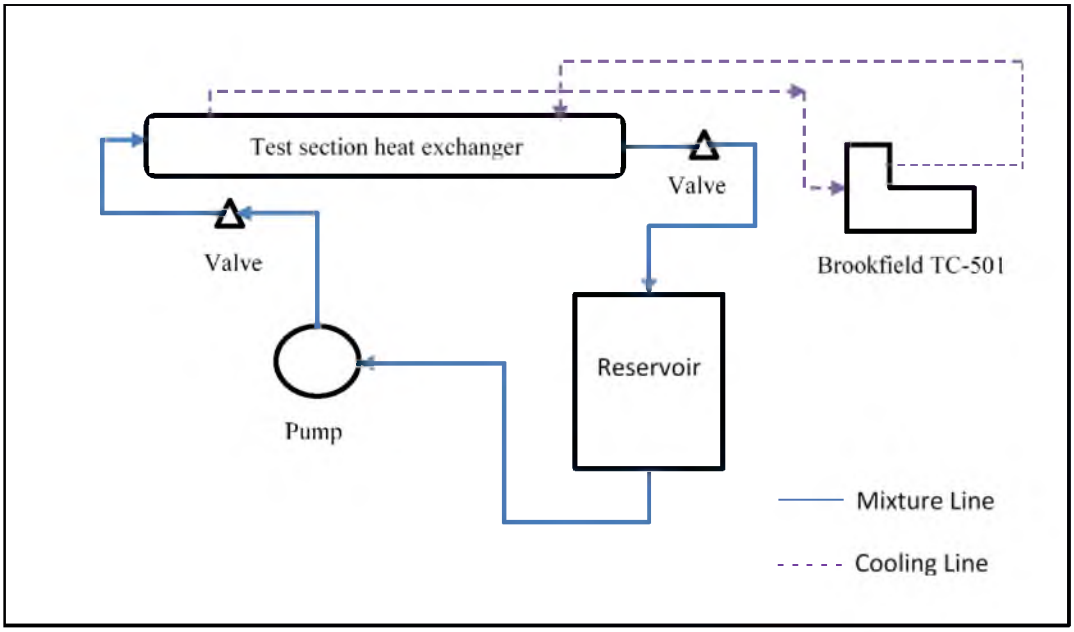

Figure 3.4. The first version of the flow loop diagram.

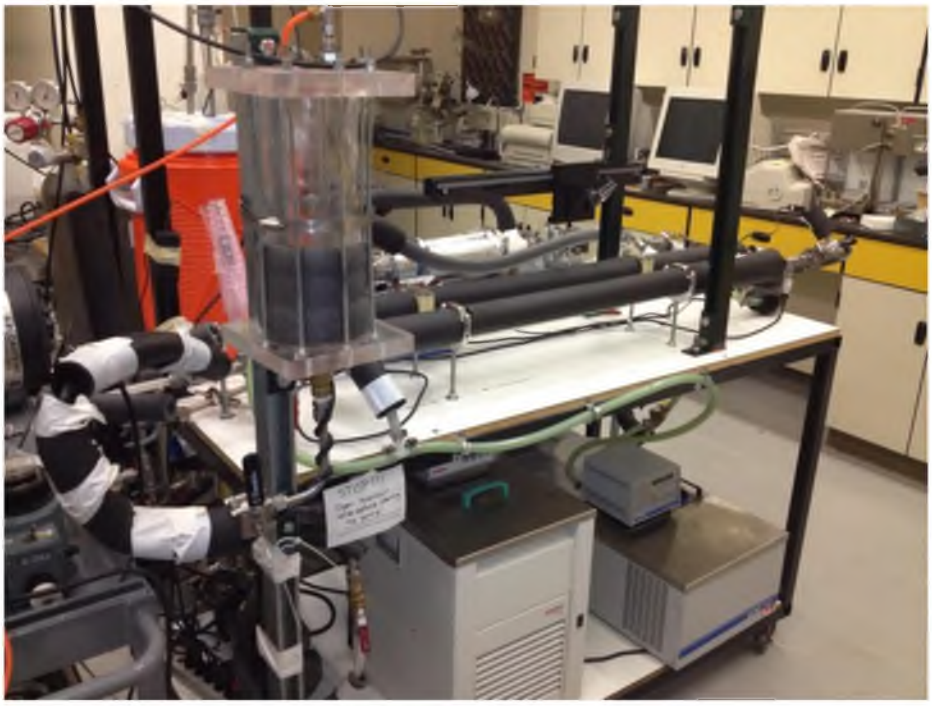

Figure 3.5. The second version of the flow loop apparatus.

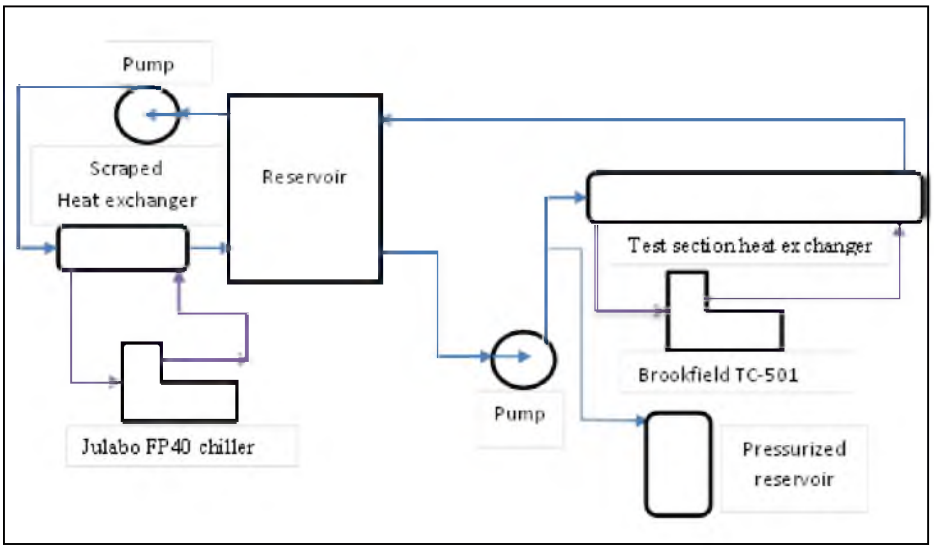

Figure 3.6. The second version of the flow loop diagram.

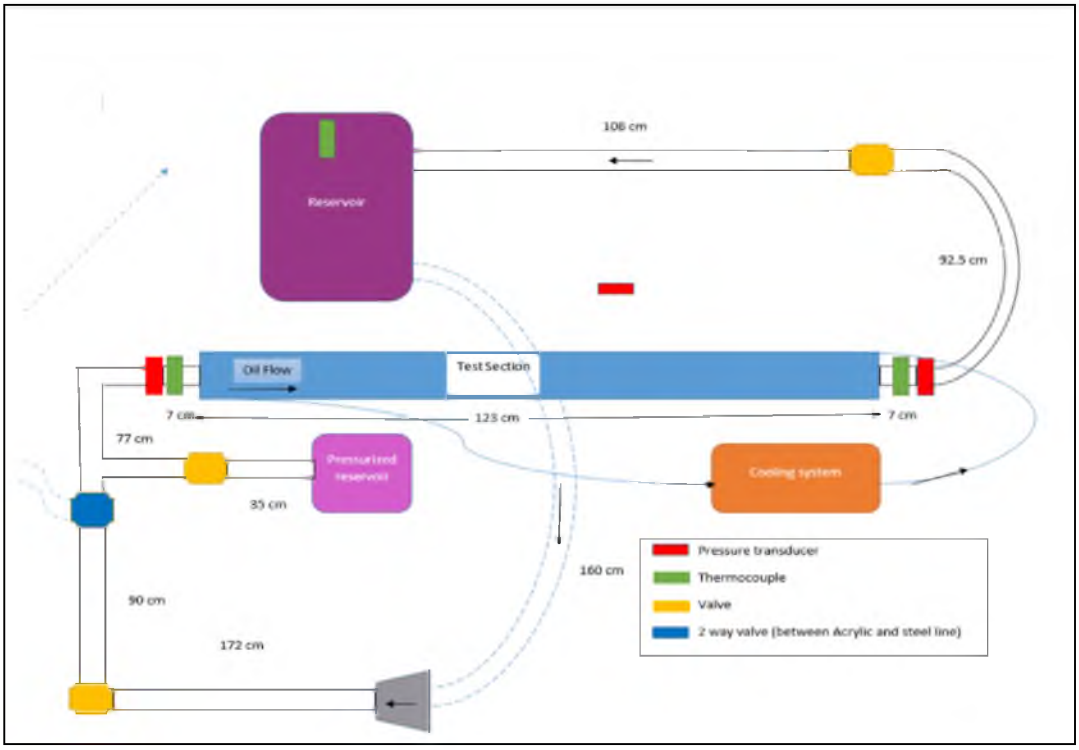

Figure 3.7. Image shows dimension of the second flow loop.

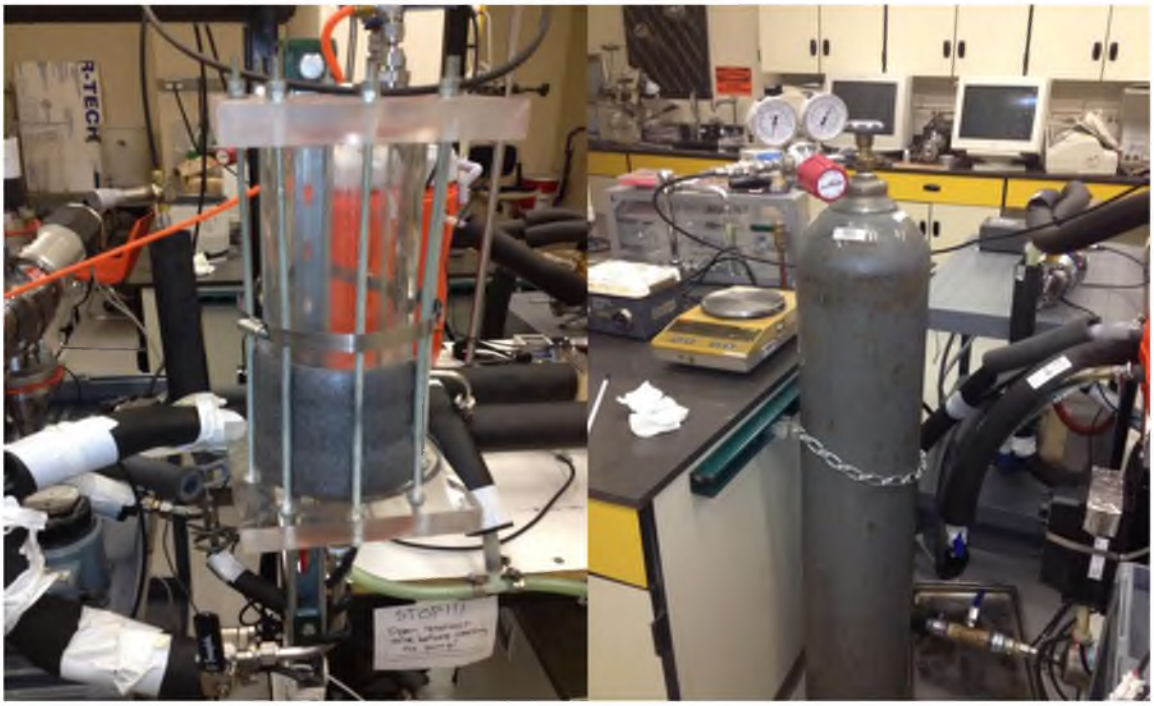

Figure 3.8. Pressurized reservoir (left) and nitrogen gas cylinder (right).

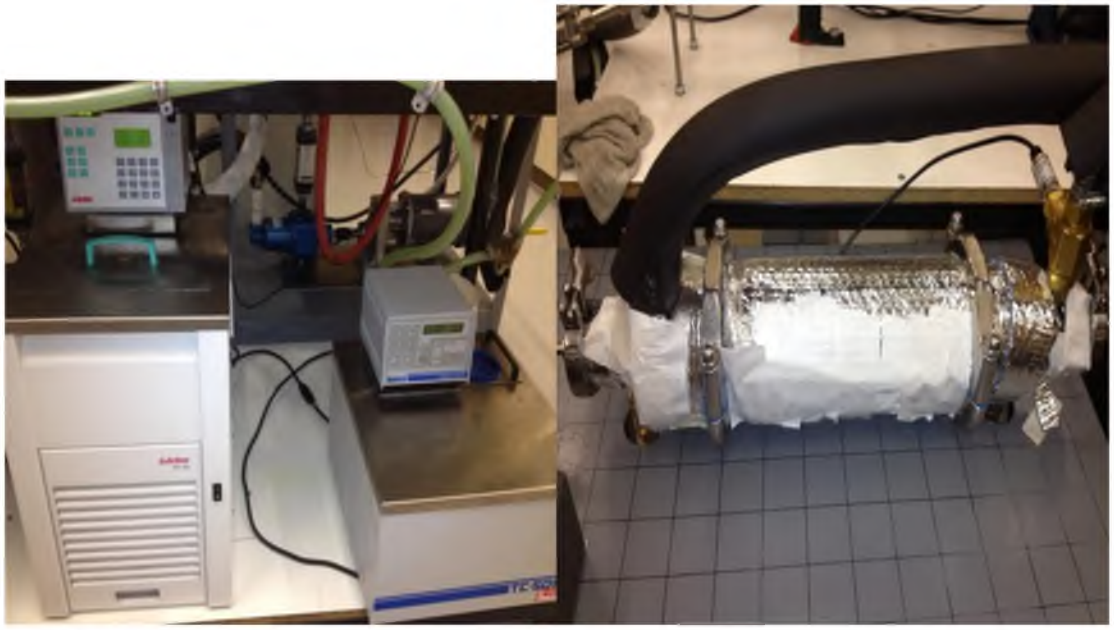

Figure 3.9. Temperature controller (left) and scraped heat exchanger (right).

Figure 3.10. Conditioning loop pump (left) and experimental loop pump (right).

Figure 3.11. Pressure transducer.

Figure 3.12. Advanced rheometer AR 500.

Figure 3.13. 2 °C cone.

Figure 3.14. Discovery HR rheometer.

Table 3.1. Flow loop second version (version 3.2) component list.

Flow loop component	Comment
Arrow Engineering 3" rotor	3" impeller used in the reservoir
Moyno 500 Sanitary pump	Progressive gravity pump used in test section
Insulated tank	Insulated tank used in oil reservoir 8 gallon
Dayton 4Z829H DC control	Speed controller for experimental pump
Brookfield TC-501	Temperature controller, pure ethylene glycol
Omega J-type thermocouple	Temperature measurement
Omega PX309-015G5V transducers	Pressure measurement in range of 0-15 psig
Omega PX309-050G5V transducers	Pressure measurement in range of 0-50 psig
Moyno 34408 pump	Progressive gravity pump used in conditioning loop
AC Tech M1105SB microconverter	Speed controller for the conditioning loop
Rex Engineering 3103	SCE blade motor, 0-5 rpm
LabVIEW software	Pressure and temperature measurement software
Dixon Sanitary clamps	SCE seal clamps
Pressurized reservoir	Gas and liquid container
Nic DAQ-9174	Data acquisition system, 4 card input
Omega HFL7102A	Flow meter, 0-2 gpm
Omega HFL7120A	Flow meter, 0-20 gpm
Swagelok fitting and tubing	1/2" and 3/4" for various components
High-density plastic tubing	1/2" for various components
Reinforced plastic hose	3/4" for pump loading and conditioning loop
Steel Test Section	0.8 cm ID, 0.5" OD, 1.5"jacket tube, stainless steel

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Flow loop results and discussions

4.1.1 First version of flow loop

Figure 4.1 shows the relationship between pressure and temperature versus time of the 7% waxy model oil cooling from 50-10 °C (0.3 °C /min) with a pressure of 4 psig. The waxy gel did not break after imposing an upstream pressure of 20 psig. The pressure was then increased by increments of 5 psig until the gel broke. The waxy gel was fractured inside the pipeline after imposing pressure at 50 psig. As shown in Figure 4.1 and 4.2, after the oil sample reaches the determined temperature of 10 °C, the gel begins to rebound after approximately 8,000 s. If the author varies the restart temperature between 10 °C, 12 °C, and 15 °C, the results demonstrate that the restart temperature affects restart pressure. Figures 4.3 and 4.4 show that the gel formed at restart temperatures of 12 °C and 15 °C, and required an upstream pressure of around 45 and 20 psig, respectively, to fracture the gel deposits inside the pipelines. Moreover, this result follows the same pattern as the 10 °C experimental condition, and the gel has a recovery point at 7,200 s. Five pressure transducers were set in different positions on the pipeline so the author could monitor any pressure drops that took place. As shown in Figures 4.5 and 4.6, at the initial period after cooling the oil sample, the pressure begins to drop relative to the axial position. Notice that upstream pressure remains constant.

This result means that some oil becomes wax, or in other words, the temperature is lower than the appearance temperature (WAT), and this leads to a pressure drop along with the axial position in the pipeline. Moreover, Figures 4.5 and 4.6 represent pressure vs. axial position as linear, so the experiment follows previous theory.

As shown in Figures 4.7 and 4.8, as the temperature reaches the shutdown temperature, the gel begins to rebound after 7300 s. The summary of the trend of the restart pressure and the restart temperature is shown in Figure 4.9.

Afterward, the author varied pressure from 4 psig to 1 psig (Figures 4.10 and 4.11) to investigate how upstream pressure conditions affect the strength of the gel. The result demonstrates that upstream pressure does not affect the strength of waxy gels, so the restart pressure does not change either. For this experiment, the oil was heated to 50 °C, and then lowered to a temperature of 25 °C while circulating to make slurry oil. It was then cooled down to 12 °C. The result is shown in Figure 4.12 for the hot flow experiment; the gel formed was broken at 45 psig. However, using the slurry method decreased the required upstream pressure to break the waxy gels to 35 psig.

For the last experiment, the author was curious as to whether the slurry condition would make any differences in waxes depositing inside the pipeline. For this experiment, the temperature was varied between 40 and 20 °C. Hot flow at 40 °C was fractured at 18 psig (see Figure 4.13), but the gel formed from slurry flow at 20 °C was broken after imposing an upstream pressure of 10 psig (see Figure 4.14). At a lower temperature the slurry condition makes the gel weaker.

4.1.2 Second version of flow loop

As mentioned earlier, the first version of the flow loop did not work well because some of the wax would deposit on the pipeline wall while the oil circulated. To solve this problem, the scraped heat exchanger was used to remove wax deposits and to make the composition of the slurry more uniform. For the second version of the flow loop, the author varied the starting temperature, restart temperature, and types of restart (hot flow restart and slurry restart).

4.1.2.1 Slurry flow restart

Three ambient restart temperatures (0 °C, 5 °C and 10 °C) were fixed in order to investigate the breaking trend. The starting temperature was also varied between WAT, 25 °C, 20 °C, 15 °C, and 10 °C. The purpose of this section is to check how much restart pressure is required to break the waxy gelled oil after shutdown.

For fixed ambient temperature at 0 °C, as shown in Figure 4.15, oil was circulated and cooled from 40 °C to the starting slurry temperature of 25 °C after heating the waxy oil up to 50 °C. After the shut in step, the waxy gel was cooled down to the desired shutdown temperature of 0 °C. The gel broke between 16.6 and 20.5 psig (measured by manually observing a pressure gauge since the limit of the pressure transducers were in the range of 0-15 psig) after increasing the upstream pressure by increments of 2 from 4 psig. On the other hand, with a starting slurry temperature of 20 °C (Figure 4.16), the gel broke between 6 and 8.2 psig. It was about 2.5 times weaker than with a starting slurry temperature of 25 °C. In Figure 4.17, the result shows that the gel was weak compared to the gel formed by the slurry conditions at 25 and 20 °C since it broke approximately a minute after opening the downstream valve. As previous theory demonstrated, the reason

that a starting slurry temperature of 25 °C was stronger than the other two conditions is because gel formed has more time for wax to deposit on the pipe wall. Thermal driving forces affect the strength of gel also. The breaking pressure of slurry flow at a fixed temperature of 0 °C is shown in Table 4.1

For fixed ambient temperature at 5 °C, As shown in Figure 4.18, oil was circulated and cooled down from 40 °C to the starting slurry temperature at WAT, and was then statically cooled down to the desired restart temperature of 0 °C. The gel broke between 36 and 40 psig (measured by manually observing a pressure gauge since the limit of the pressure transducers are in the range of 0-15 psig) after increasing the upstream pressure by increments of 2 from 4 psig. For the starting slurry temperature of 20 °C (see Figure 4.19), the gel broke between 5.5 and 7.9 psig. The gel formed for this restart temperature was approximately 78% weaker than the WAT starting temperature.

Figures 4.20 and 4.21 show the restart pressures required to break the gel formed at the starting slurry temperature of 20 and 15 °C, respectively. The results show that the gel was very weak. With starting slurry temperature of 20 °C the gel broke between 3.9 and 5.5 psig. The gel formed from 15 to 5 °C suddenly broke after opening the experimental downstream valve. The breaking pressure of slurry flow at a fixed temperature of 5 °C, shown in Table 4.2, and the slurry restart pressure trend at a fixed temperature in the last two conditions as marked "N/A" in Table 4.2. It can be predicted that the gel is a lot weaker than the condition of starting slurry temperature at 15 °C and the gel broke right away after opening the downstream valve.

For fixed ambient temperature at 10 °C, for this experiment, oil was circulated and cooled from 40 °C to starting slurry temperature at 25 °C and was cooled down to the

desired shut down temperature of 10 °C. The gel was very weak for this restart temperature. It broke right away after opening the downstream valve. The results are shown in Figures 4.23 and 4.24. It was concluded that the gel would be even weaker for starting slurry temperatures of 20, 15, and 10 °C, so the gel was expected to break at or below 4 psig. The breaking pressure of slurry flow at a fixed temperature of 10 °C is shown in Table 4.3.

4.1.2.2 Hot flow restart

To demonstrate the effectiveness of the slurry restart method, it was important to perform hot flow restart test, so comparisons could be made. The restart ambient temperature was kept the same for both slurry flow and hot flow, so that the results would show the effect of restart type between slurry restart and hot flow restart.

The shutdown temperatures do not affect the restart pressure of a gel if both of them are above WAT. For example, gels formed from shutdown temperatures of 40 °C (see Figure 4.25) and 30 °C (see Figure 4.26) varied little in the restart pressure required to break them. They both broke between approximately 36 and 40 psig (manually observing a pressure gauge). In similar fashion, for a restart temperature of 5 °C, the two conditions of starting temperature at 40 and 30 °C (see Figures 4.27 and 4.28, respectively), which are above WAT, did not have any effect on the restart pressure. The reason is because wax starts precipitating and deposits to the pipe wall when the temperature is below WAT (27 °C for this waxy oil), so it has no effect on the restart pressure.

Another series of experiments with hot flow involved changing the restart temperature. By varying the desired restart temperature between 5, 10, 12, and 15 °C, it

was found that the gel was weakest at a restart temperature of 15 °C. It broke between 5.4 and 6.3 psig (see Figure 4.29). For a starting temperature of 12 °C, the gel broke between 12.1 and 14.7 psig (see Figure 4.30), which is approximately two times stronger than the condition with a starting temperature of 15 °C. Basically, breaking pressure increases as the restart temperature decreases, which is shown in Table 4.4. Figure 4.31 represents the hot flow breaking trend.

4.2 Rheometer results and discussions

4.2.1 Hot flow restart (using an AR 500 rheometer)

The rheometer was mostly used to measure gelation temperature and yield stress in these experiments. In the same fashion as the flow loop, the restart temperature was fixed at 10 °C, and the three starting temperatures were varied between 40, 35 and 30 °C (see Figure 4.32 - 4.34, respectively). All of these temperatures are above WAT and did not affect the yield stress. The reason is similar to the flow loop experiments. It is because wax starts precipitating and forming a gel structure only when the temperature is below WAT, which is 27 °C for this waxy oil. The yield stress of hot flow restart at 10 °C was between 80-100Pa. Figure 4.35 shows the oscillation tests that reveal the gelation temperature of the oil. These tests were carried out at a cooling rate of 0.3 °C/ min with a frequency of 0.02 Hz and a shear stress of 0.8 Pa. They both had a gelation temperature between 22 and 23 (the temperature at which the elastic modulus reaches the viscous modulus).

4.2.2 Slurry flow restart (using an AR 500 rheometer)

Because the correlation between the rheometer and the flow loop was a major part of this research, the slurry method in the rheometer was very similar to the slurry method

used in the flow loop. To set up slurry at the desired starting temperature, a flow experiment was used in order to constantly shear the oil and make it slurry. This method can prevent the formation of waxy gels while the temperature is below WAT.

Slurry restart was compared with hot flow restart in order to see the effects of the method. The slurry method was started by heating the oil sample to 40 °C where it is still a pure liquid. The sample was then cooled down while flowing to the desired slurry temperature. Finally, the sample was statically cooled to the defined restart temperature.

Slurry restarts at 10 °C, which were statically cooled from 25 and 20 °C, have a lower yield stress compared to the hot flow restart at 10 °C. The yield stress of the hot flow restart at 10 °C was between 80 and 100 Pa. In comparison, the slurry yield stress of static cooling from 25 °C to 10 °C was between 60 and 80 Pa.

The creep test was started at 40 Pa, and was increased by increments of 20 Pa. The gel had an elastic yield stress from 40-60 Pa because the gel was in creep state for 1 minute, as shown in Figure 4.36 for creep test at 60 Pa.

After imposing a stress of 80 Pa (see Figure 4.37), the gel started to break. This means the yield stress of the gel was between 60 and 80 Pa, which was 2 times weaker than the hot flow case. As the author expected, the slurry yield stress from 20 °C to 10 °C (see Figures 4.38-4.40) was even weaker compared to the hot flow case. The gel broke between 10 and 15 Pa, which was 7-8 times weaker than the hot flow case.

4.2.3 Hot flow and slurry flow restart at a fixed temperature of 5 °C (using a Discovery HR rheometer)

Since the AR 500 rheometer did not work well for low temperature conditions, a Discovery HR rheometer was used for experiments requiring temperatures lower than 10

°C. Figure 4.41 shows the WAT of the gel. The WAT was about 26-27 °C, which is indicated by the first temperature where the slope of line changes unexpectedly. Figures 4.42 to 4.46 show a series of creep tests performed on a gel formed by statically cooling from 20 to 5 °C. The gel did not break after applied stresses of 5, 10, 15, and 20 Pa, respectively. They were in a creep stage, and the compliance value (inverse of stress) increased slowly. The gel finally broke after a 25 Pa was imposed, so this means that the yield stress of this slurry restart condition was between 20 and 25 Pa.

In the case of slurry restart from 25 to 5 °C, the WAT of the gel was about 26-27 °C (Figure 4.47). The gel did not break after applying stresses less than 50 Pa (Figure 4.48). It was in a creep stage where strain slowly increased and partially recovered. In other words, the elastic yield stress was determined to be 50 Pa. The gel finally broke after imposing a stress of 80 Pa (Figure 4.49). The yield stress of a slurry restart from 25 to 5 °C was between 50 and 80 Pa.

Comparing yield stresses with the other cases at slurry temperatures of 15 and 10 °C, showed that the gel formed was much weaker than a slurry temperature of 25 °C. Figures 4.50 and 4.51 show creep and recovery tests with a slurry condition of 15 to 5 °C, The gel broke at an applied stress of 8 Pa (Figure 4.52) after imposing stress from 2, 5 to 8 Pa. Figure 4.53 shows that the gel has a WAT equal to 26-27 °C. Static cooling from 10 to 5 °C is the weakest condition, the gel broke between 1 and 2 Pa. The gel crept for 60 s and recovered for 30 s (Figure 4.54). One interesting point was that the gel always broke after the strain exceeded 1 % as shown in Figure 4.55 at 2 Pa.

Hot flow restart at a condition of 40 to 5 °C was compared with other slurry flow restarts. The first 60 s of the curve in Figure 109 at 50 Pa of applied stress shows the

time-dependent shear strain of the gel in the creep stage, and then gives a shear stress equal to zero after 60 s in creep stage. The last 30 s of the curve in Figure 4.56 shows the recovery strain of the gel. The gel partially recovers since the strain dropped back to 0.025%. It continued in a creep state after imposing a shear stress of 80, 100, and 120 Pa (see Figures 4.57-4.59). Finally, at constant stress of 150 Pa as shown in Figure 4.60, the strain curve demonstrates fracture-like behavior when the strain reaches about 1%. Thus, the static yield stress value of the gel was in the range of 120-150 Pa. Hot flow and slurry restart at a fixed temperature of 5 °C is shown in Table 4.5.

4.3 Correlation between flow loop and rheometer

Lastly, the relationship between the flow loop and rheometer was studied in order to find a correlation. Restart pressure from the flow loop was converted to yield stress by Eq.1 or Eq. 2, which were reported by previous researchers.

$$\tau_S = 0.5\,R\left(-\frac{dP}{dZ}\right)$$

Or

$$\Delta P_{min} = 2\frac{L\tau_S}{R}$$

where, test section length (L) = 123 cm, Radius of pipe (R) is 0.4 cm, L/D = 307.5, pressure drop ΔP is determined from the restart pressure from the flow loop, and τ_S is static yield stress.

The correlations between flow loop and rheometer at a fixed temperature of 5 and 10 °C are shown in Table 4.6 and 4.7, respectively. It is demonstrated that the yield stress from the flow loop had an over predicted value compared to the rheometer for most conditions, especially for the hot flow restart method. On the other hand, this meant that

the breaking pressure obtained by converting the static yield stress measured from rheometer measurements under predicted the actual flow loop results. This is contrary to what previous researchers have found.

Figure 4.61 shows a summary of the relationship between restart pressure and shutdown temperature at a fixed restart temperature of 5 °C. One significant observation was that the restart pressure dropped rapidly from the temperature above WAT (27 °C) to 25 °C. A temperature difference of only 2 degrees made an obvious change in the restart pressure required to break the gel. This agreed well with previous research done by Bidmus and Mehrotra [20]. Wax usually precipitates and deposits to the wall mostly when the temperature of the gel is closest to WAT, so the 2 degree difference in temperature near the WAT zone can affect the strength of the gel significantly. On the other hand, a small temperature difference did not affect the strength of the gel that much when far away from WAT zone. As shown in Figure 4.62, the static yield stress from the rheometer showed a trend similar to the flow loop. The yield stress remains constant at 120-180 Pa if the sample is above WAT, and then it decreases rapidly at the slurry temperatures of 25 °C (2 °C below), which has a yield stress of 50-80 Pa. The static yield stress was not affected significantly when the slurry temperature was near the restart temperature.

Comparison between actual yield stress from the rheometer and predicted yield stress from the flow loop for slurry restart is shown in Figure 4.63. The two curves have similar trends, but differ by a constant value. Unfortunately, the constant upstream pressure applied was greater than the breaking pressure for slurry temperatures at or below 15 °. Slurry flow restart methods can reduce the restart pressure required to break

gel deposits in the pipeline when compared to hot flow restart methods. For example, a slurry temperature of 20 °C required a pressure between 4 and 6 psig to break the gel. On the other hand, hot flow restart required a restart pressure between 36 and 40 psig. The breaking pressure was 6-10 times weaker when using the slurry flow method. Similarly, for rheometric measurements, the static yield stress for a slurry temperature of 20 °C is approximately 5-12 times weaker than the hot flow case since the yield stress of a slurry temperature at 20 °C was between 15 and 25 Pa, and was between 120 and 180 Pa for hot flow.

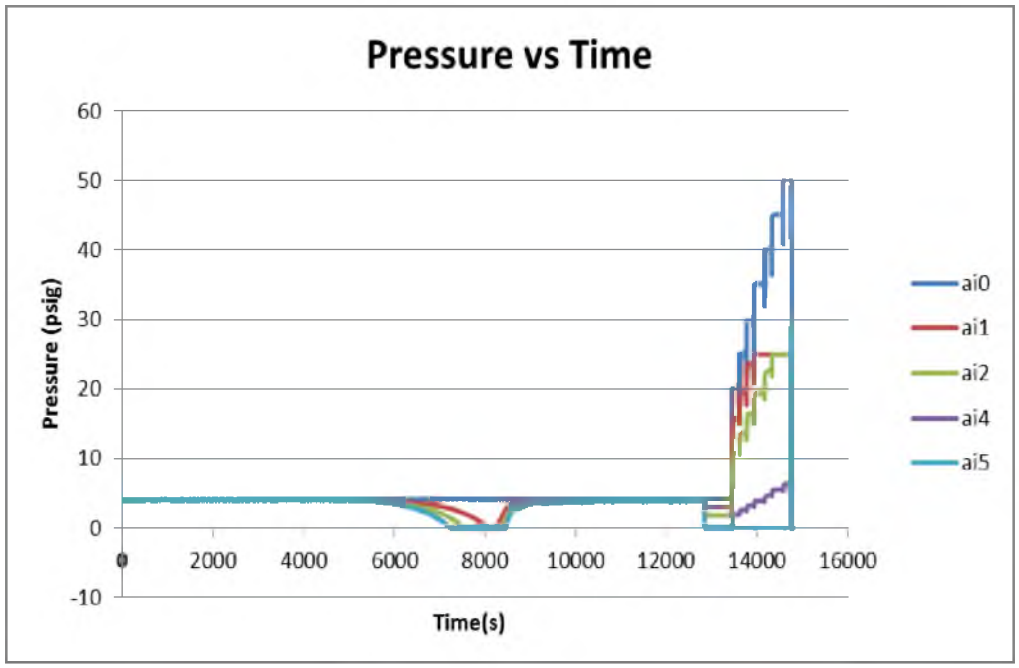

Figure 4.1. The relationship between pressure and time of 7% waxy model oil cooled down from 50-10 °C (0.3 °C /minute) with a pressure of 4 psig.

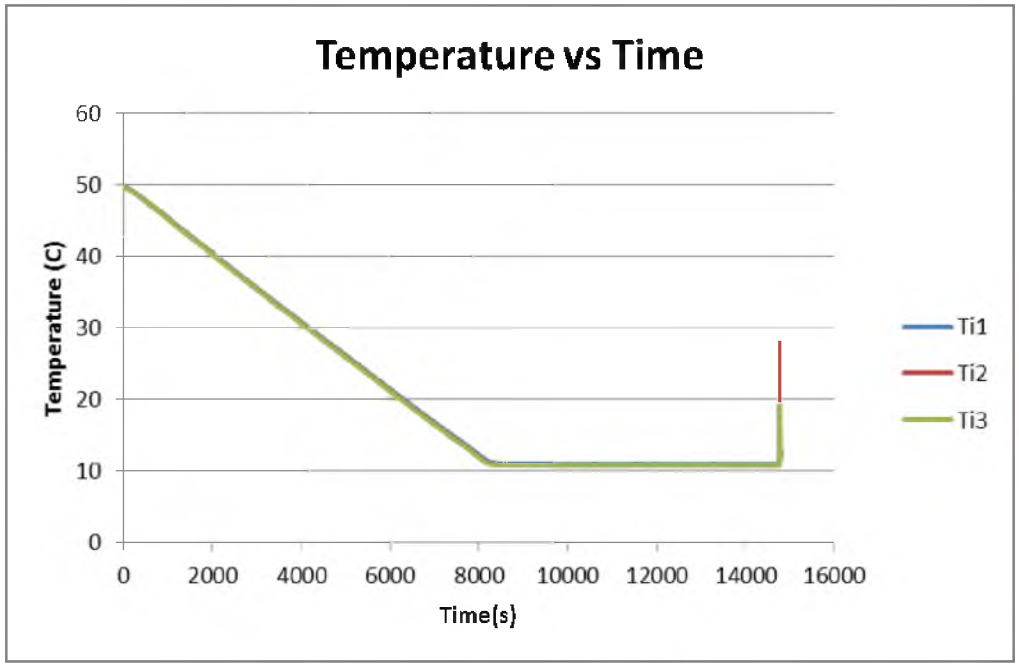

Figure 4.2. The relationship between temperature and time of 7% waxy model oil cooled down from 50-10 °C (0.3 °C/minute) with a pressure of 4 psig.

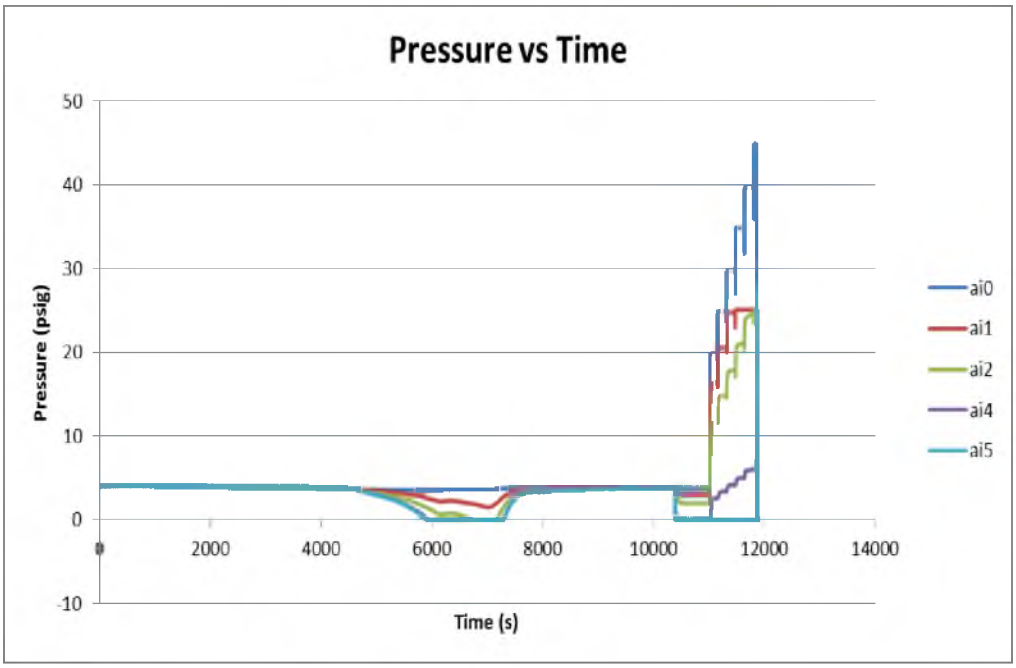

Figure 4.3. Seven percent waxy model oil cooled from 50-12 °C (0.3 °C/minute) with a pressure of 4 psig, waxy gels were fractured inside the pipeline after imposing pressure at 45 psig.

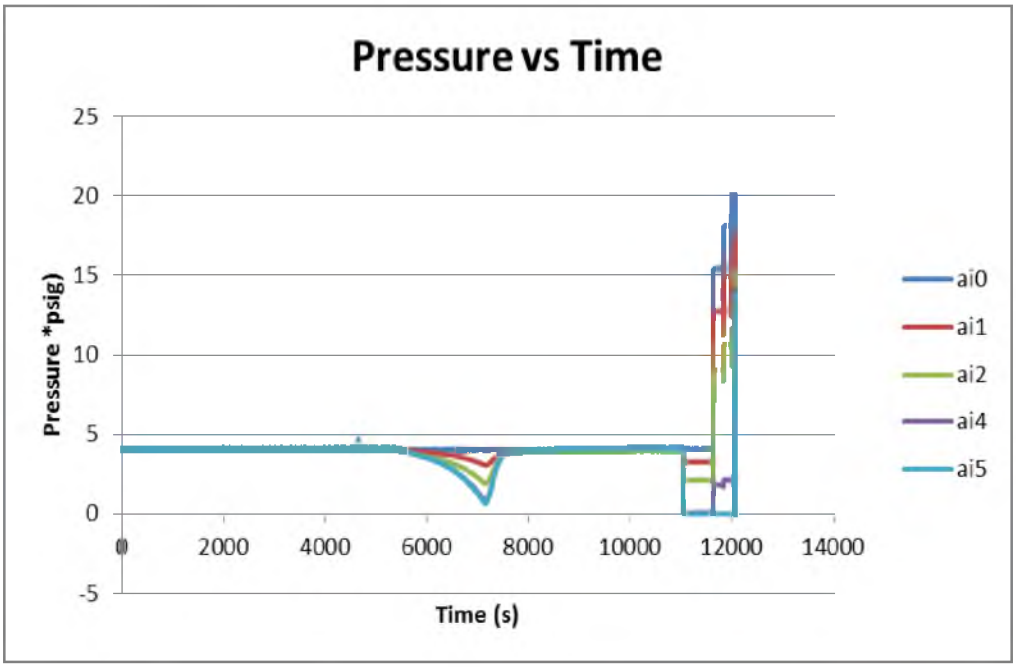

Figure 4.4. Seven percent waxy model oil cooled from 50-15 °C (0.3 °C/minute) with a pressure of 4 psig, waxy gels were fractured inside the pipeline after imposing pressure at 20 psig.

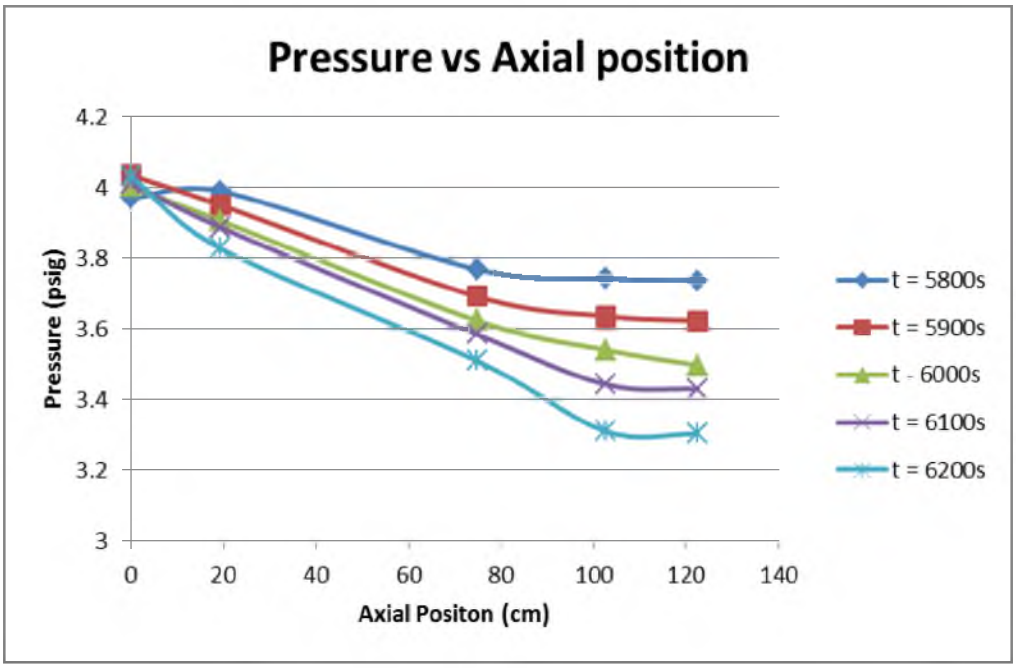

Figure 4.5. Relationship between pressure and axial position for 7% waxy model oil cooled from 50-15 °C (0.3 °C/minute) with a pressure of 4 psig. The data were collected at the initial time of the cooling period.

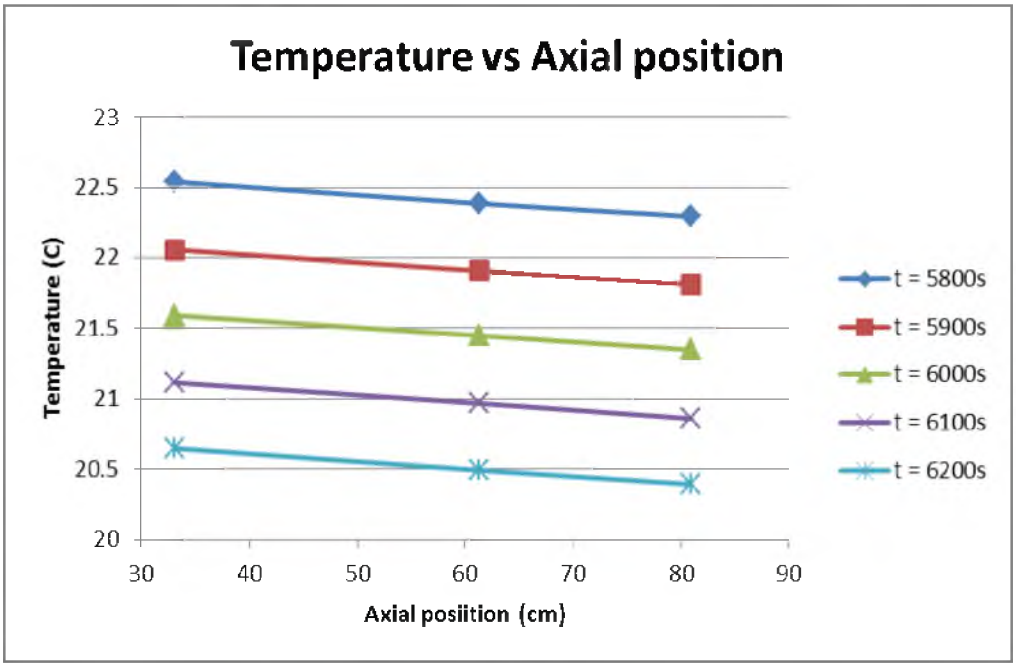

Figure 4.6. Relationship between temperature and axial position for 7% waxy model oil cooled from 50-15 °C (0.3 °C/minute) with a pressure of 4 psig. The data were collected at the initial time of the cooling period.

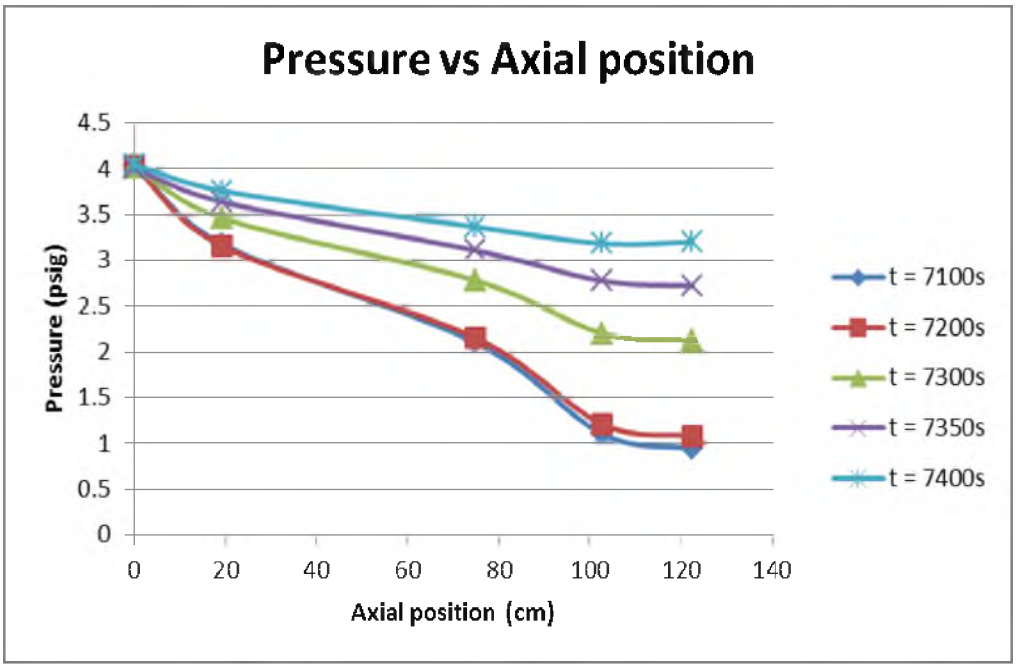

Figure 4.7. Relationship between pressure and axial position for 7% waxy model oil cooled down from 50-15 °C (0.3 °C/minute) with a pressure of 4 psig. The data were collected after the gel reached a steady temperature.

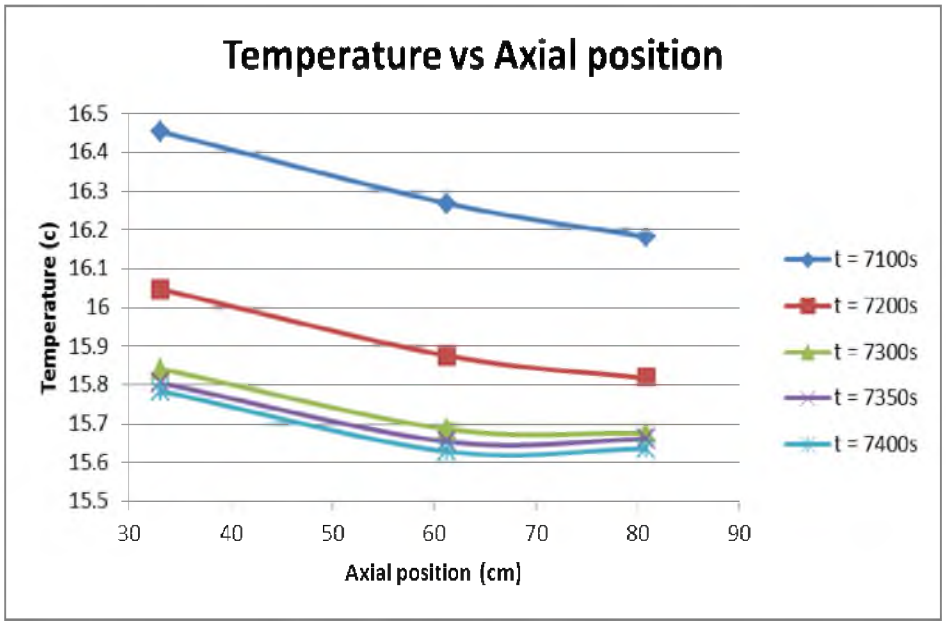

Figure 4.8. Relationship between temperature and axial position for 7% waxy model oil cooled down from 50-15 °C (0.3 °C/minute) with a pressure of 4 psig. The data were collected after the gel reached a steady temperature.

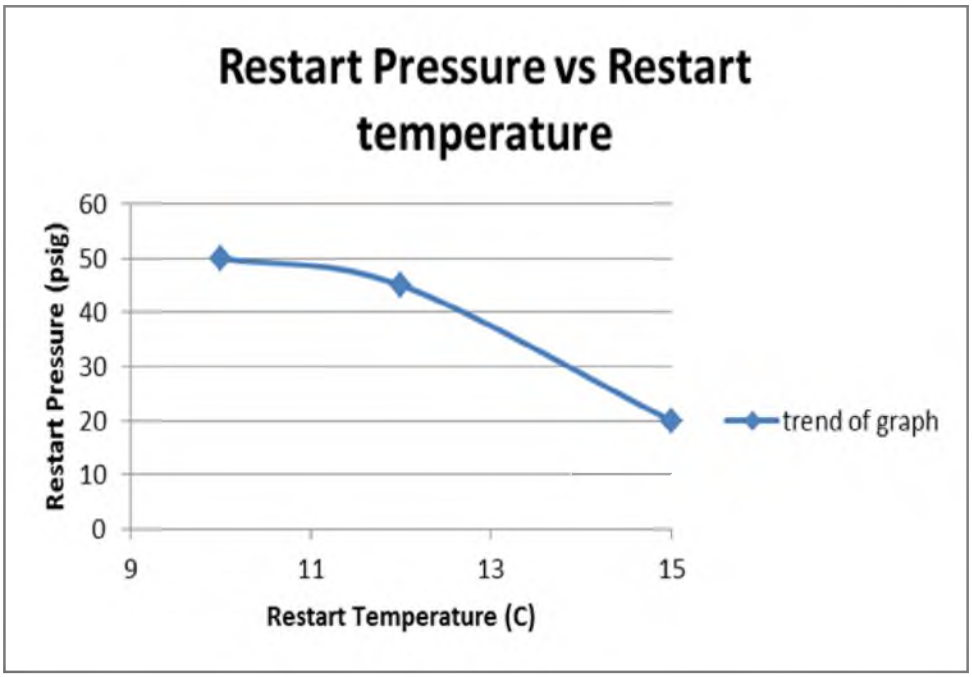

Figure 4.9. Relationship between restart pressure and restart temperature.

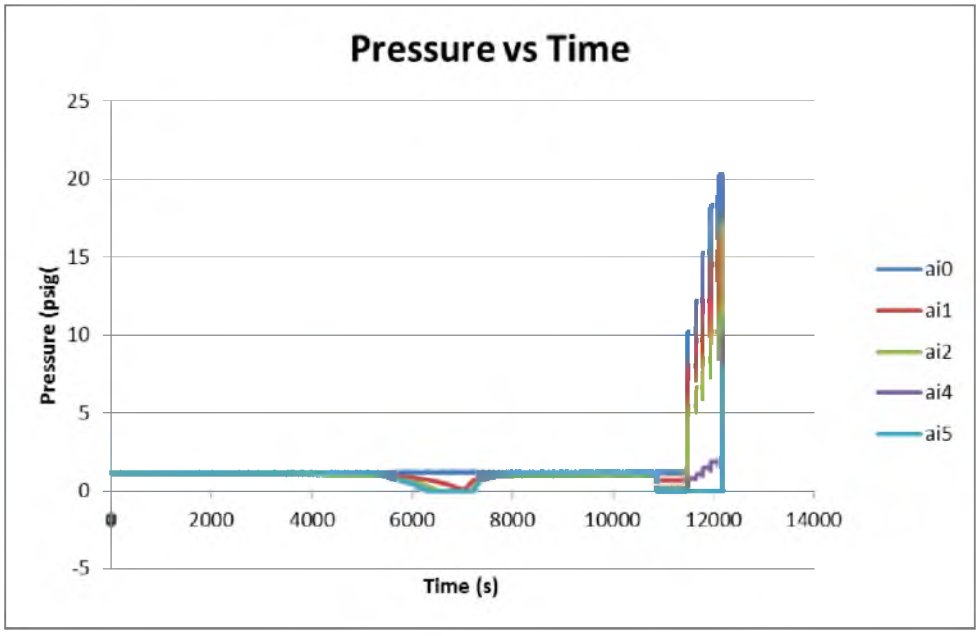

Figure 4.10. The relationship between pressure and time for 7% waxy model oil, cooled down from 50-15 °C (0.3 °C/minute) with a pressure of 1 psig.

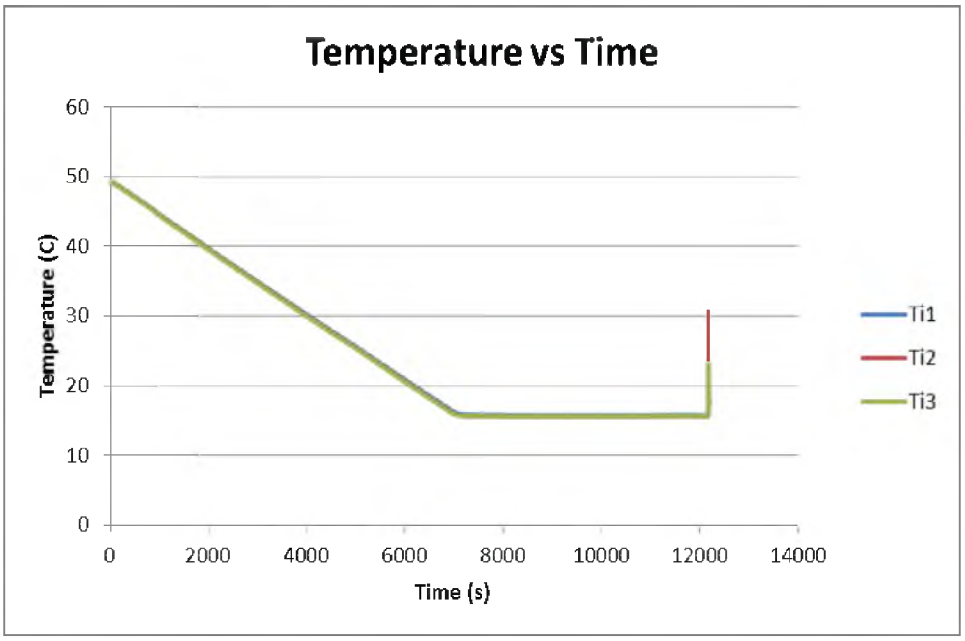

Figure 4.11. The relationship between temperature and time for 7% waxy model oil cooled down from 50-15 °C (0.3 °C/minute) with a pressure of 1 psig.

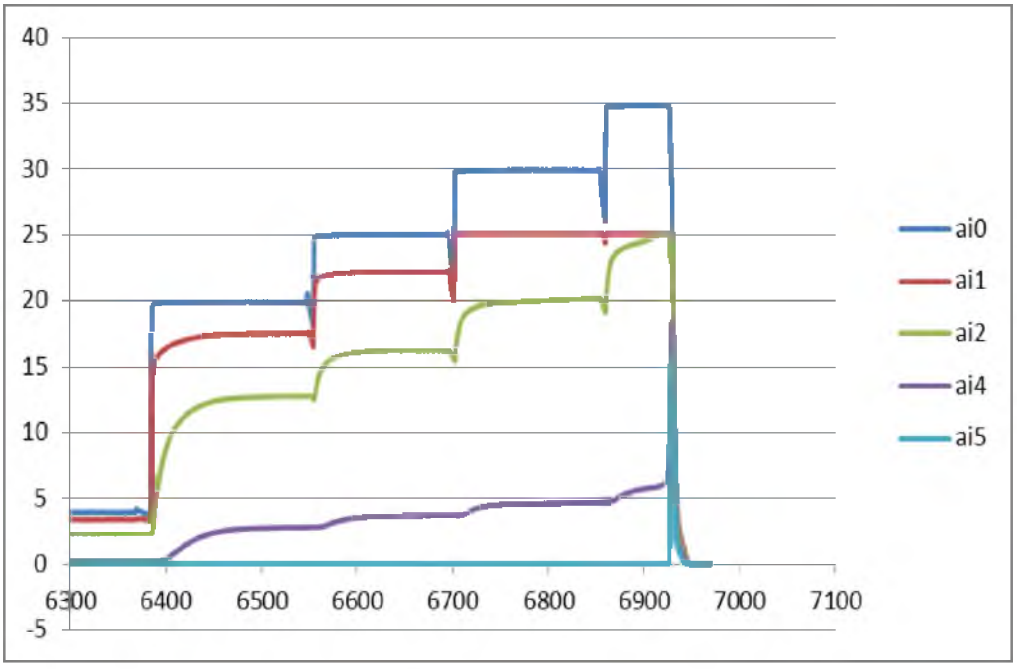

Figure 4.12. The relationship between pressure and time for 7% waxy model oil slurry at 25 °C and cooled down from 25-12 °C (0.3 °C/minute) with a pressure of 4 psig.

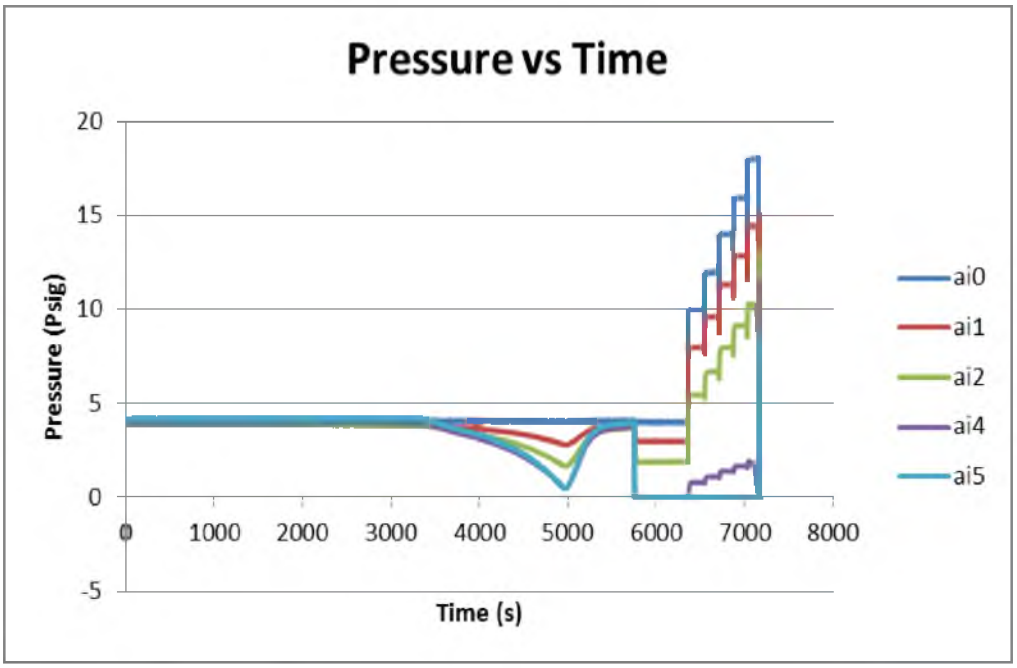

Figure 4.13. Hot flow condition from 40 °C to 15 °C, 0.3 °C per minute.

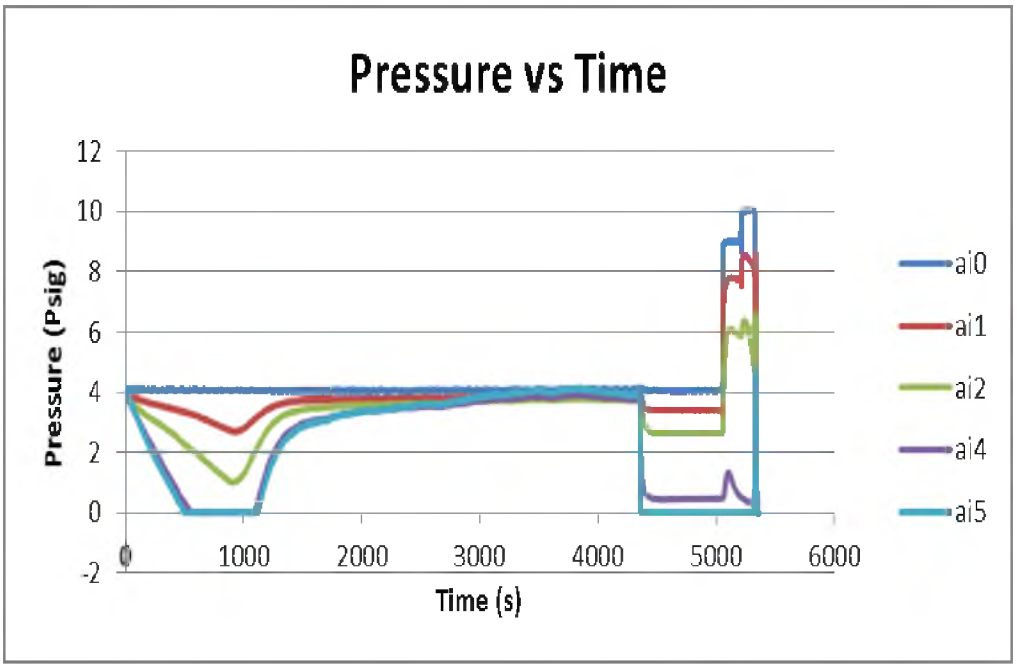

Figure 4.14. Slurry flow condition from 20 °C to 15 °C, 0.3 °C per minute.

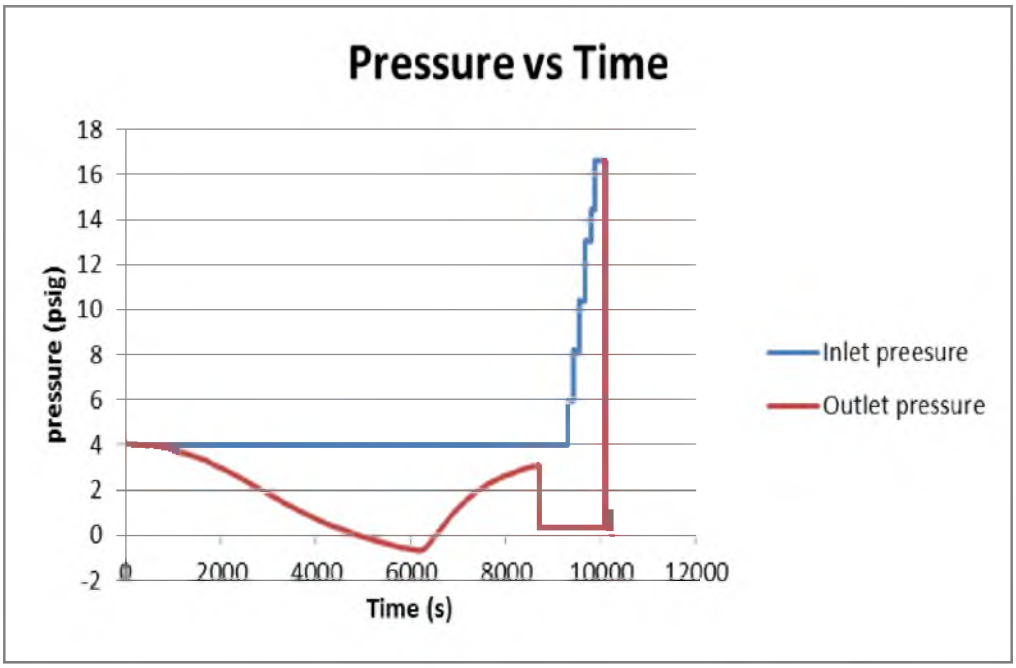

Figure 4.15. Applied an up stream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 0 °C (0.3 °C per minute). *The gel broke between 16.6 and 20.5 psig.

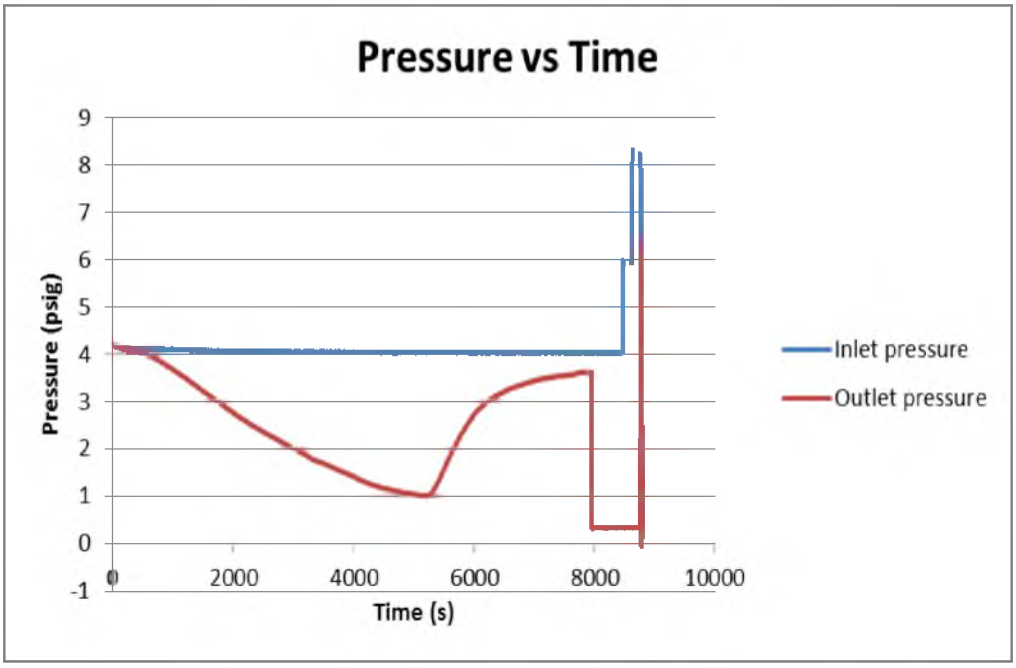

Figure 4.16. Applied an up stream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 0 °C (0.3 °C per minute).

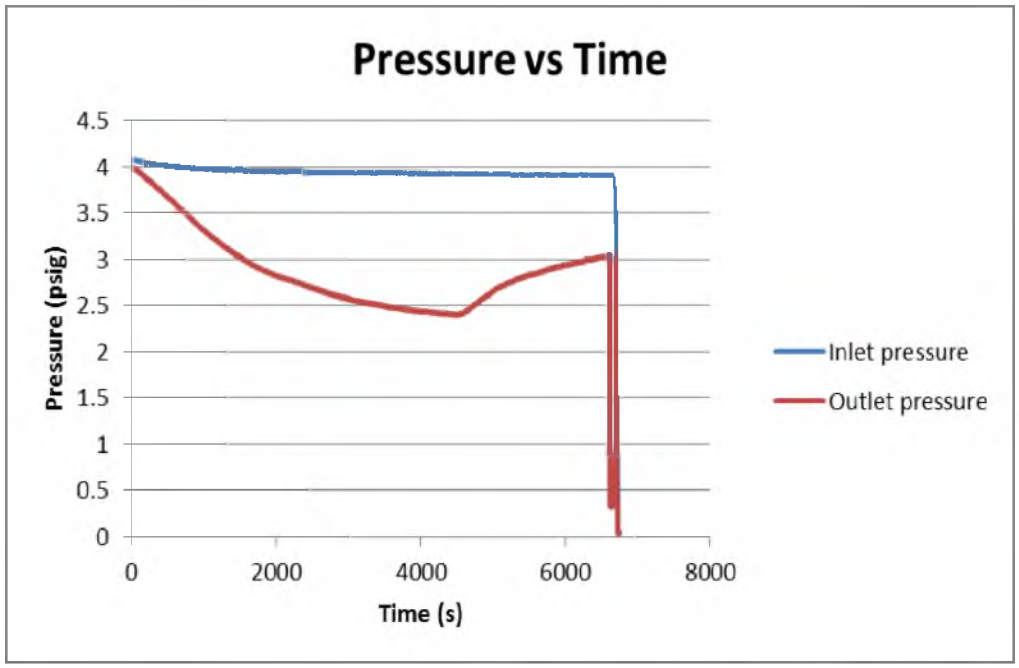

Figure 4.17. Applied an up stream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 0 °C (0.3 °C per minute).

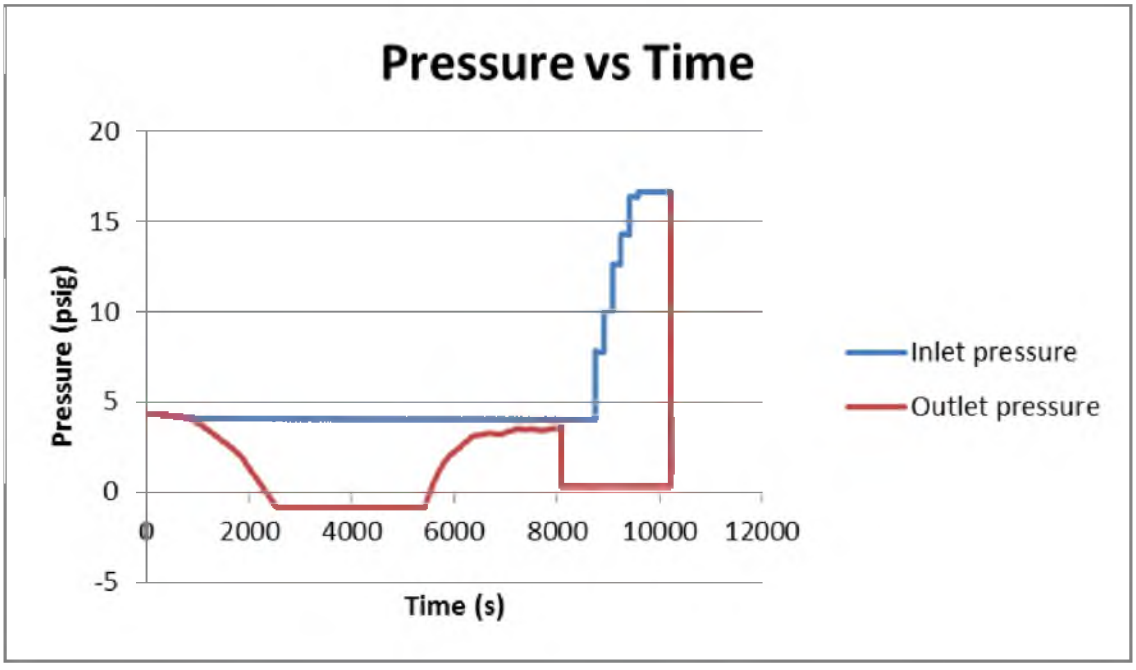

Figure 4.18. Applied an up stream pressure of 4 psig with a slurry condition at WAT (27 °C) and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36.3 and 40.5 psig (measured by manually observing a pressure gauge).

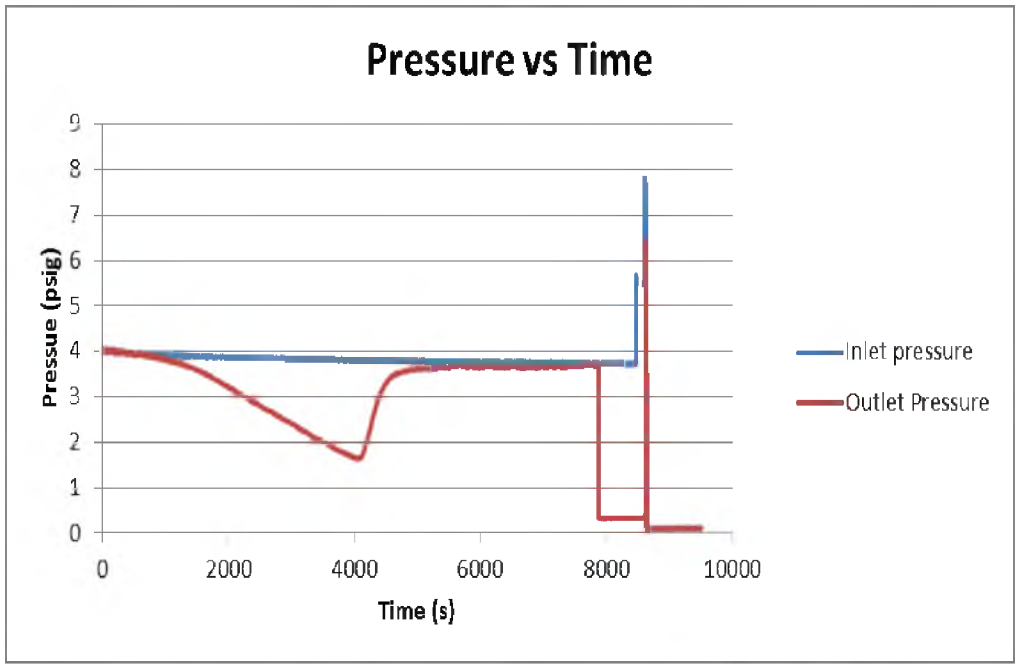

Figure 4.19. Applied an up stream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 5 °C (0.3 °C per minute).

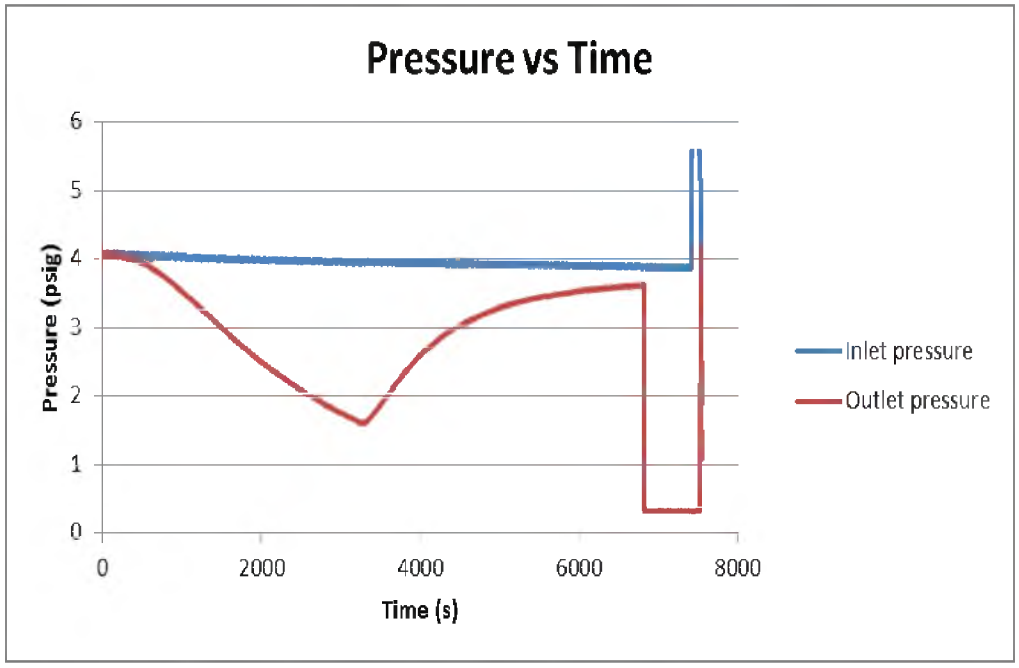

Figure 4.20. Applied an up stream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 5 °C (0.3 °C per minute).

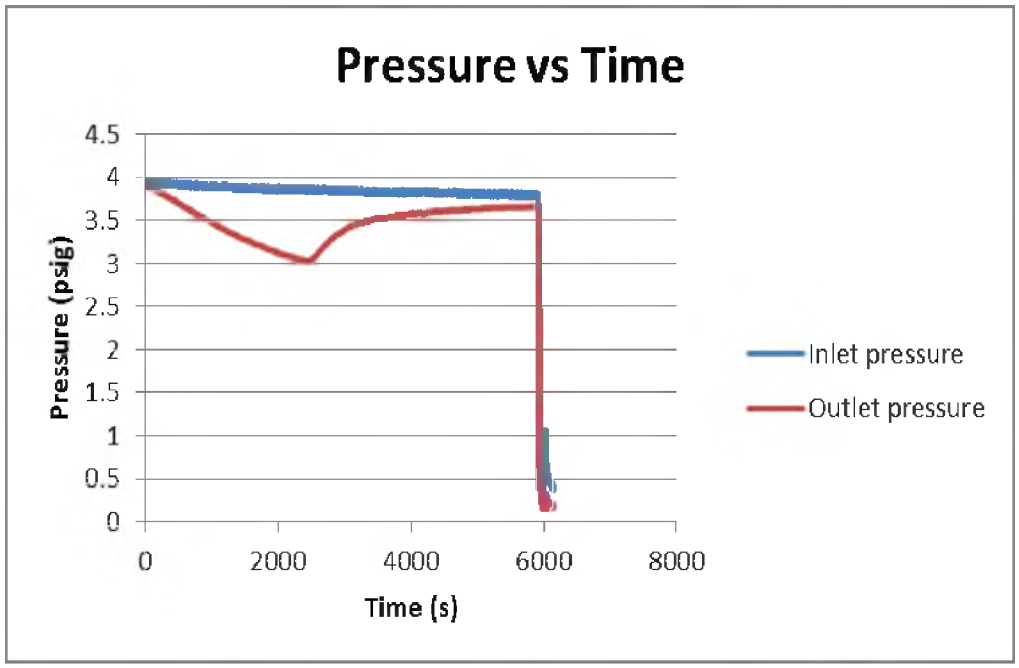

Figure 4.21. Applied an up stream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 5 °C (0.3 °C per minute.

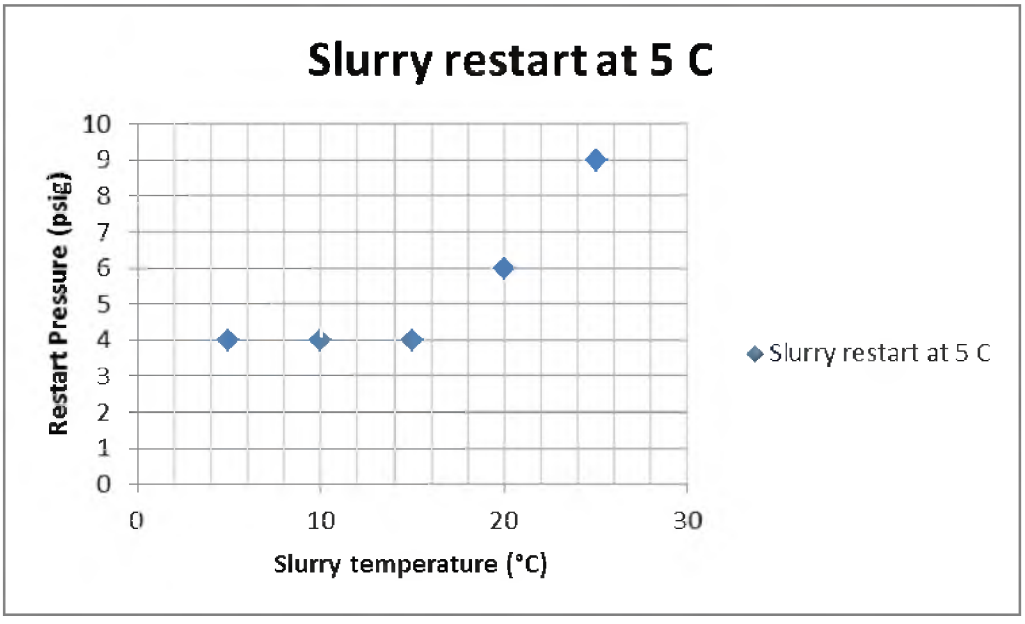

Figure 4.22. Slurry restart pressure trend at a fixed ambient temperature of 5 °C.

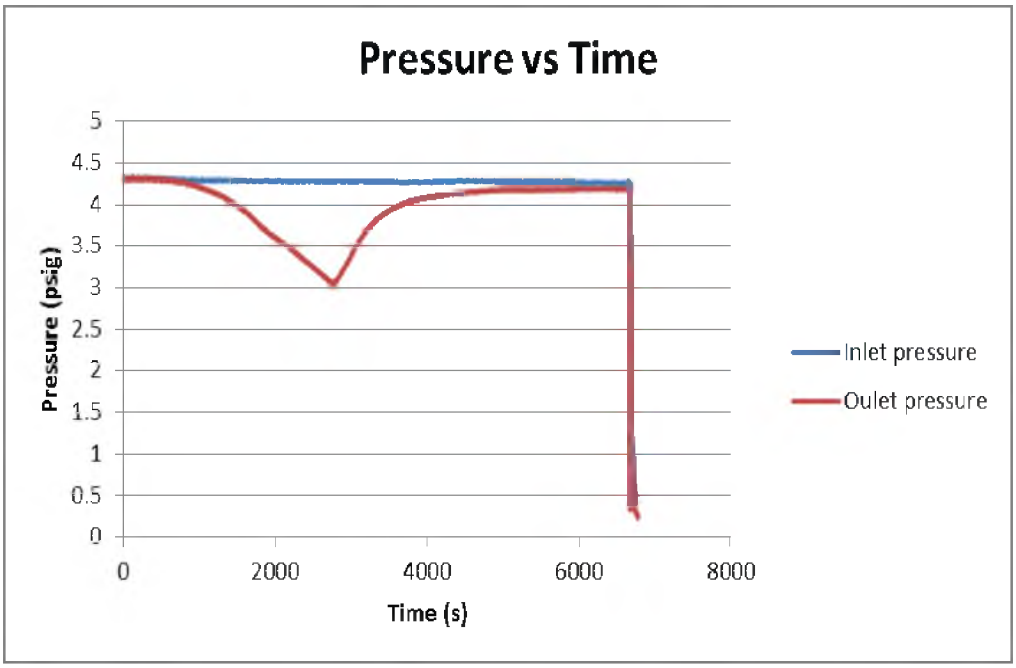

Figure 4.23. Run number 1. Applied an up stream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 10 °C (0.3 °C per minute).

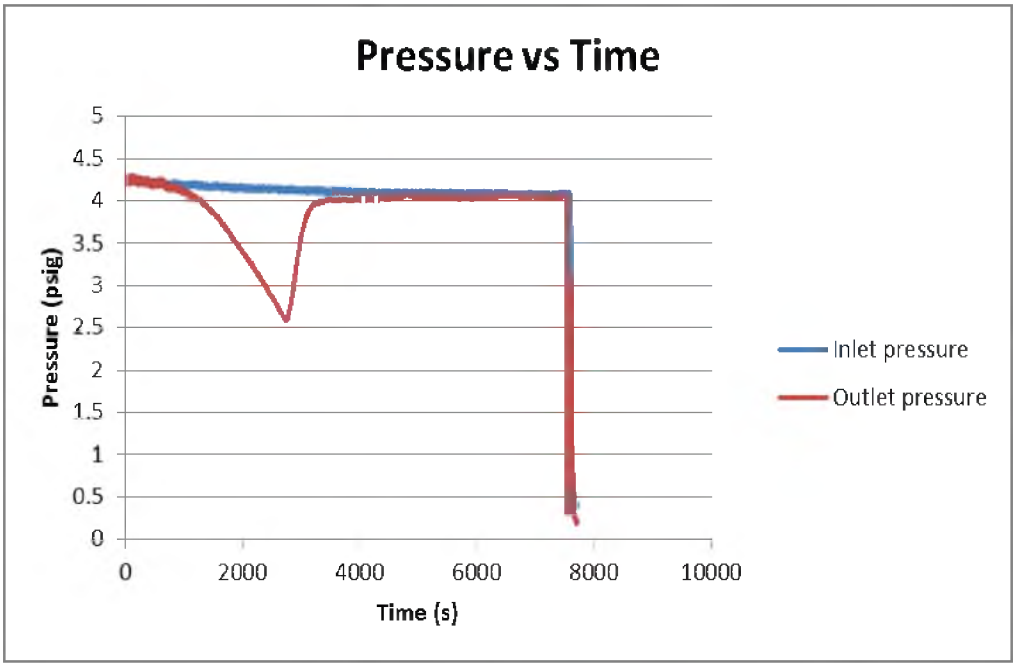

Figure 4.24. Run number 2. Applied an up stream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 10 °C (0.3 °C per minute).

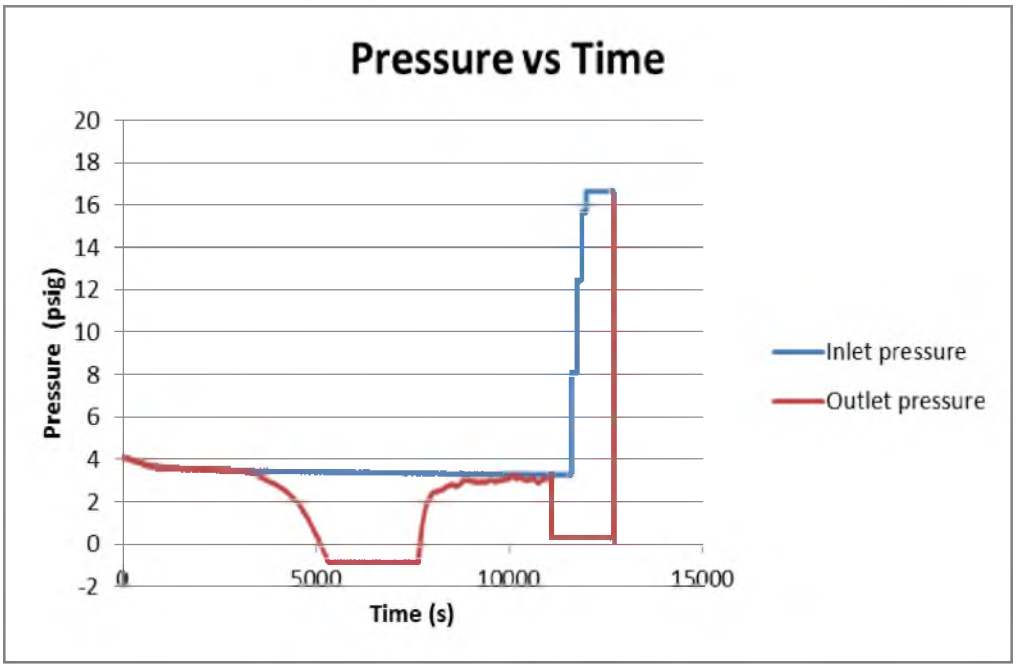

Figure 4.25. Applied an up stream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36.3 and 40.5 psig (measured by manually observing a pressure gauge).

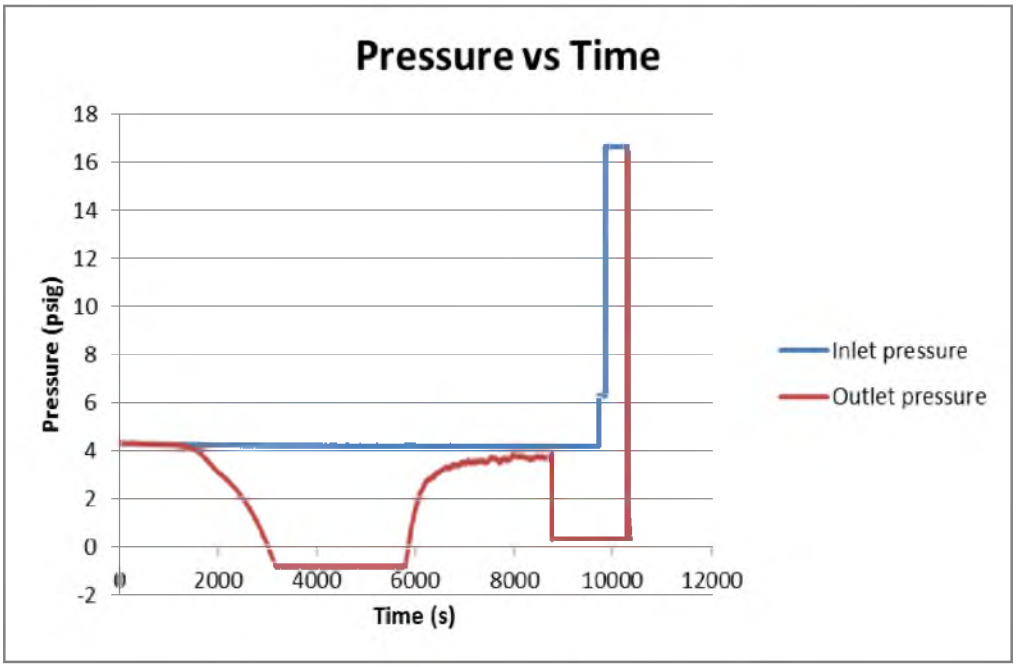

Figure 4.26. Applied an up stream pressure of 4 psig with a hot flow condition at 30 °C and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36 and 40.7 psig (measured by manually observing a pressure gauge

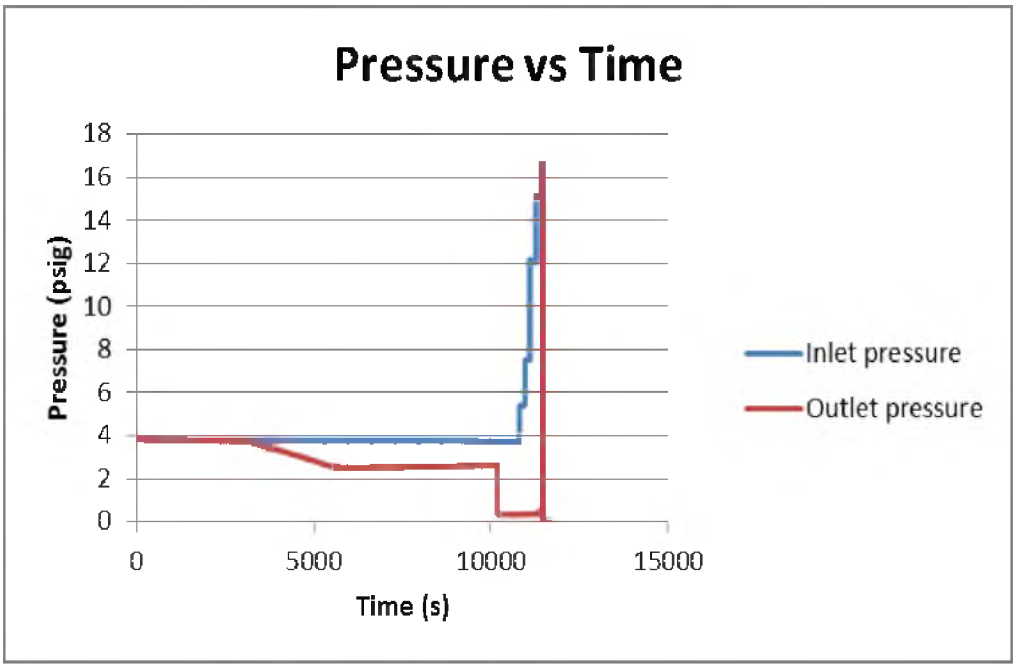

Figure 4.27. Applied an up stream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 15.5 and 20.1 psig (measured by manually observing a pressure gauge).

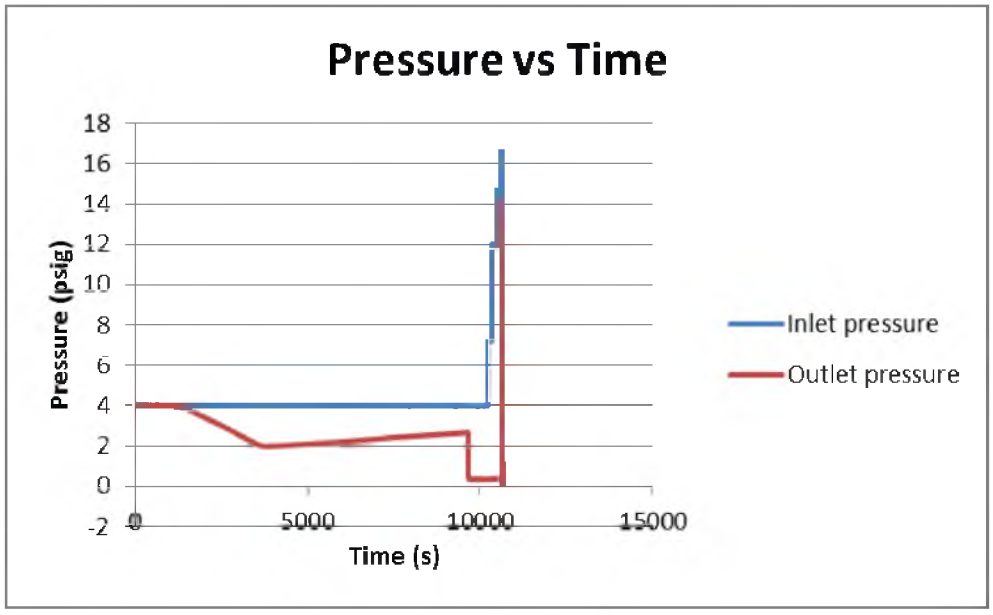

Figure 4.28. Applied an up stream pressure of 4 psig with a hot flow condition at 30 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 16.6 and 20.2 psig (measured by manually observing a pressure gauge).

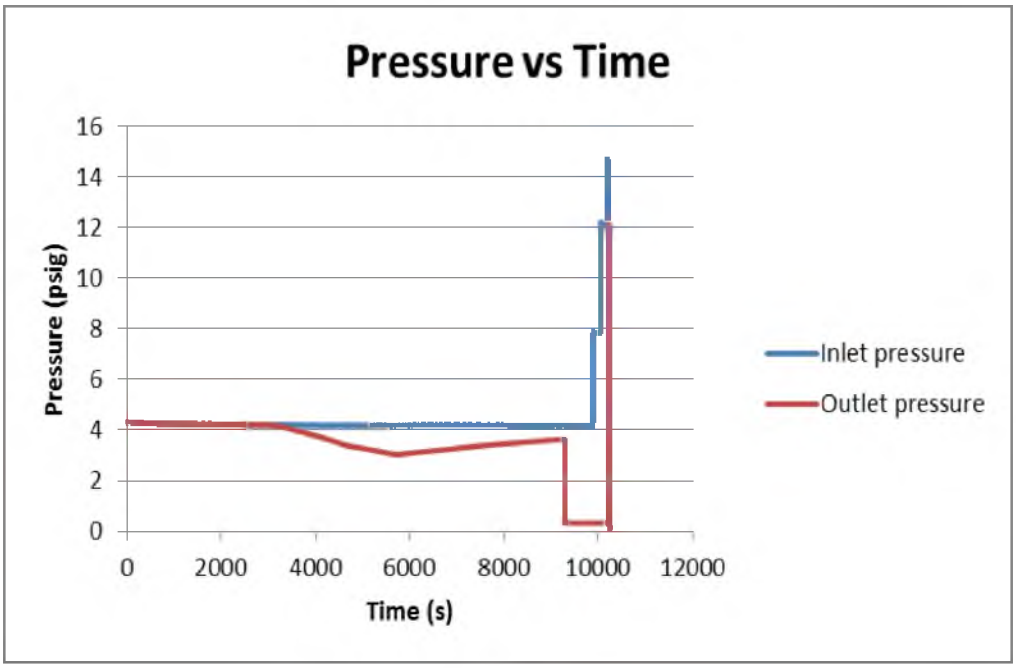

Figure 4.29. Applied an up stream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 12 °C (0.3 °C per minute).

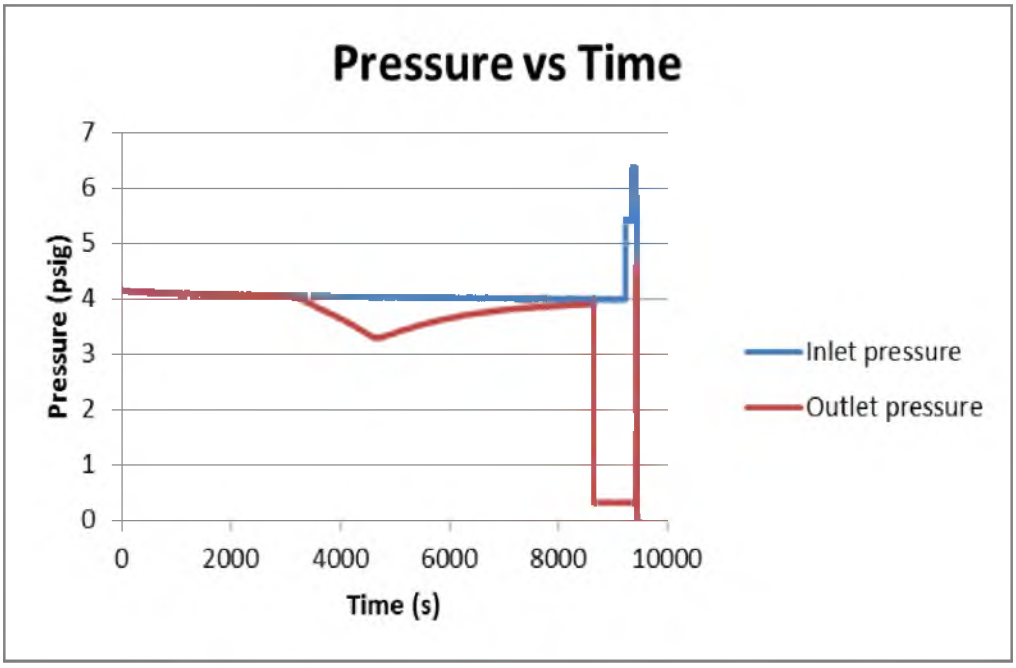

Figure 4.30. Applied an up stream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 15 °C (0.3 °C per minute).

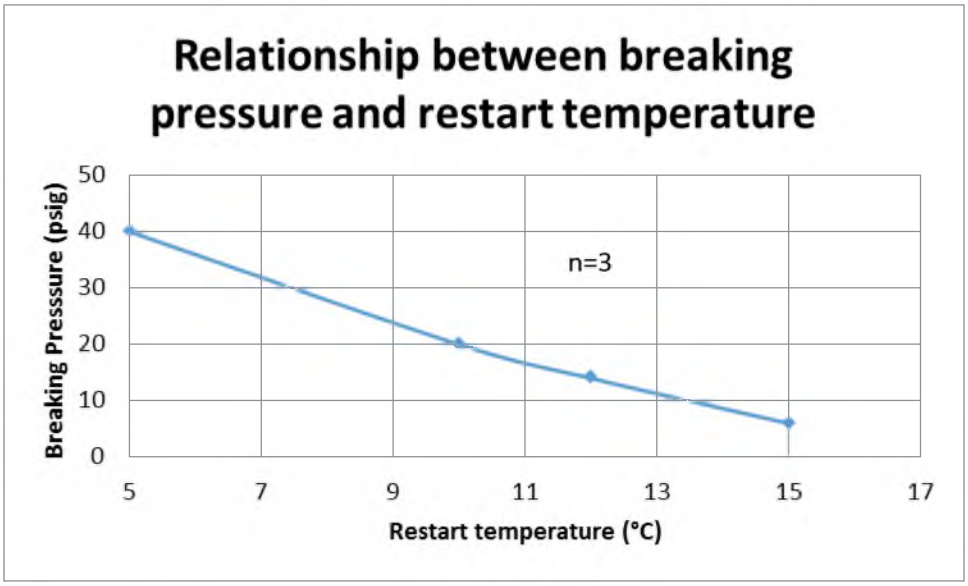

Figure 4.31. Hot flow restart pressure trend with static cooling from 40 °C.

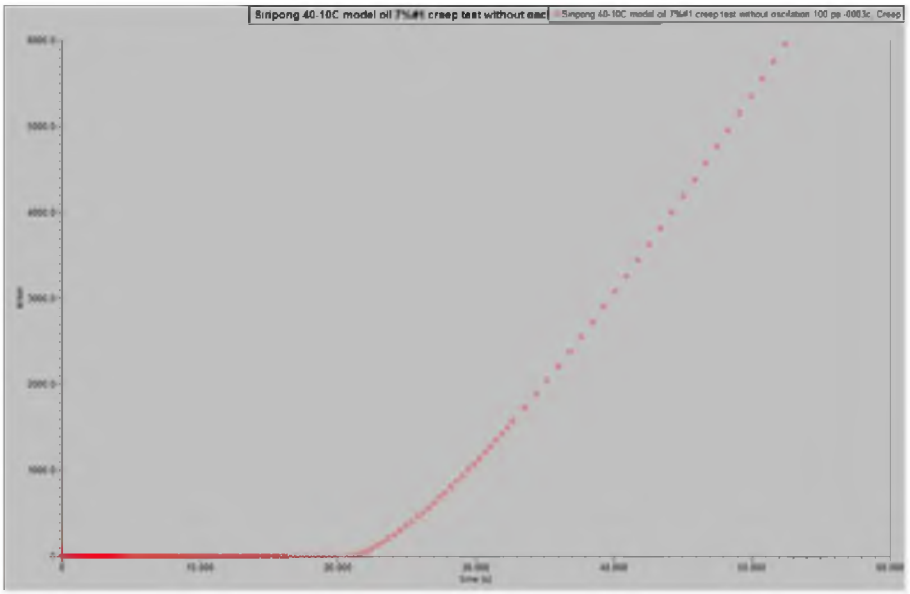

Figure 4.32. Creep test at 100 Pa, Condition: 40-10 °C without oscillation, 0.3 °C per minute.

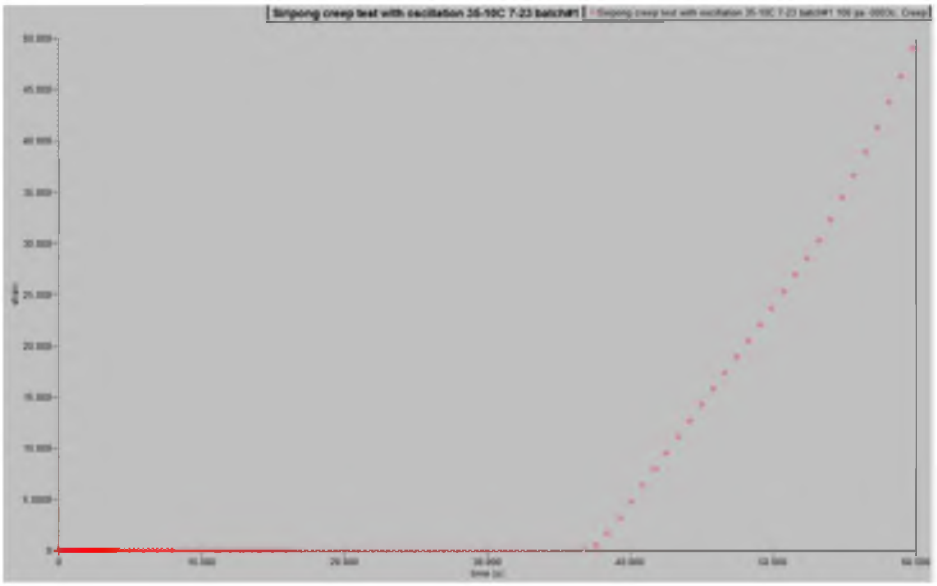

Figure 4.33. Creep test at 100 Pa, Condition: 35-10 °C without oscillation, 0.3 °C per minute

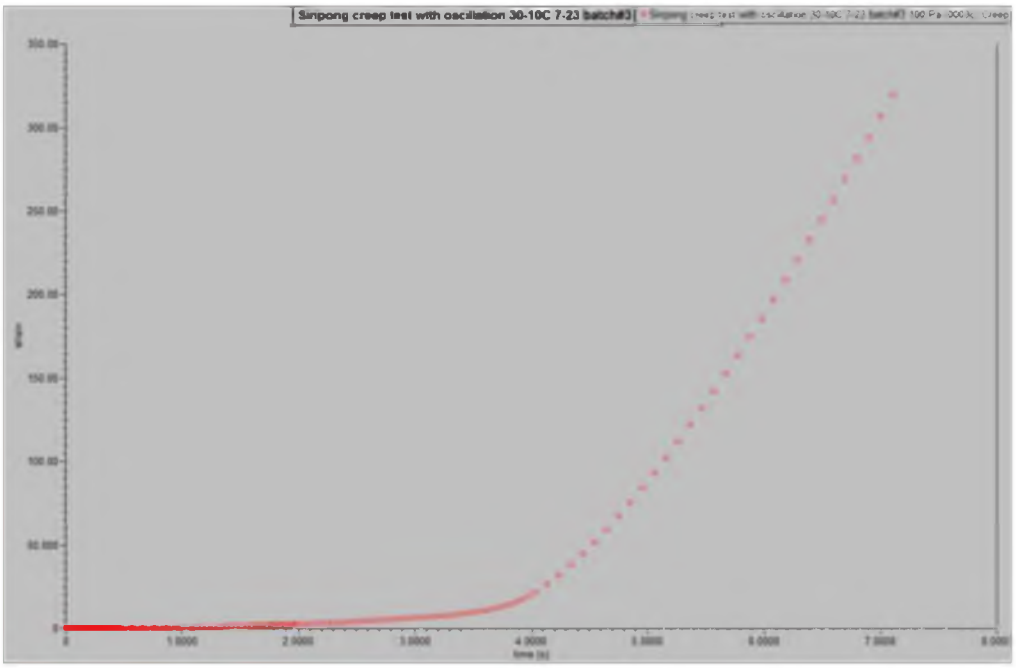

Figure 4.34. Creep test at 100 Pa, Condition: 30-10 °C without oscillation, 0.3 °C per minute.

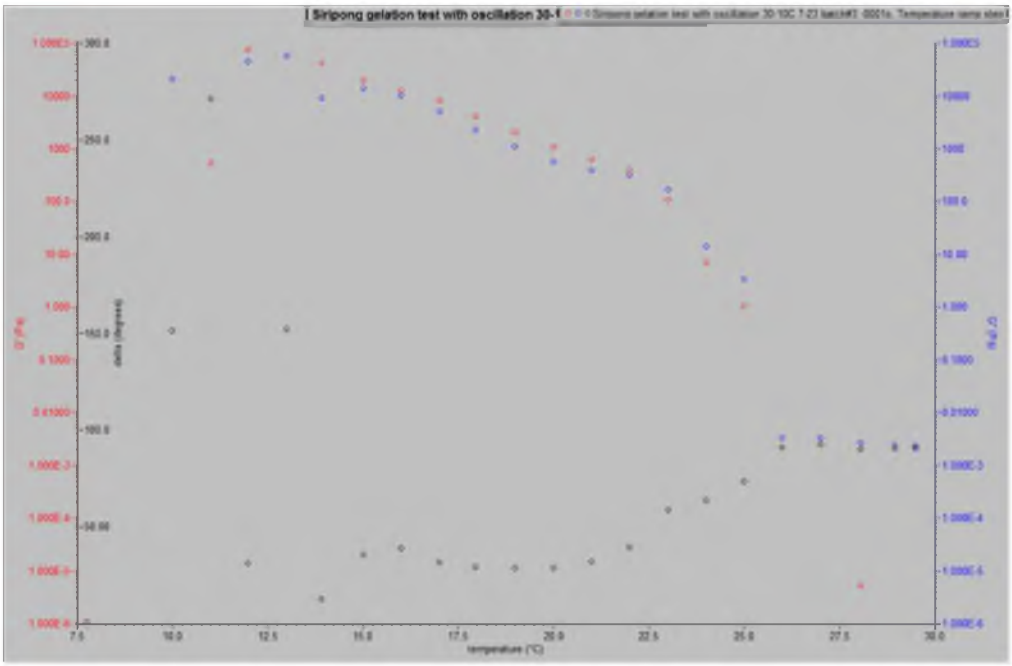

Figure 4.35. Gelation test condition: 30-10 °C with oscillation**,** 0.3 °C per minute, shear stress 0.8 Pa, frequency 0.02 Hz.

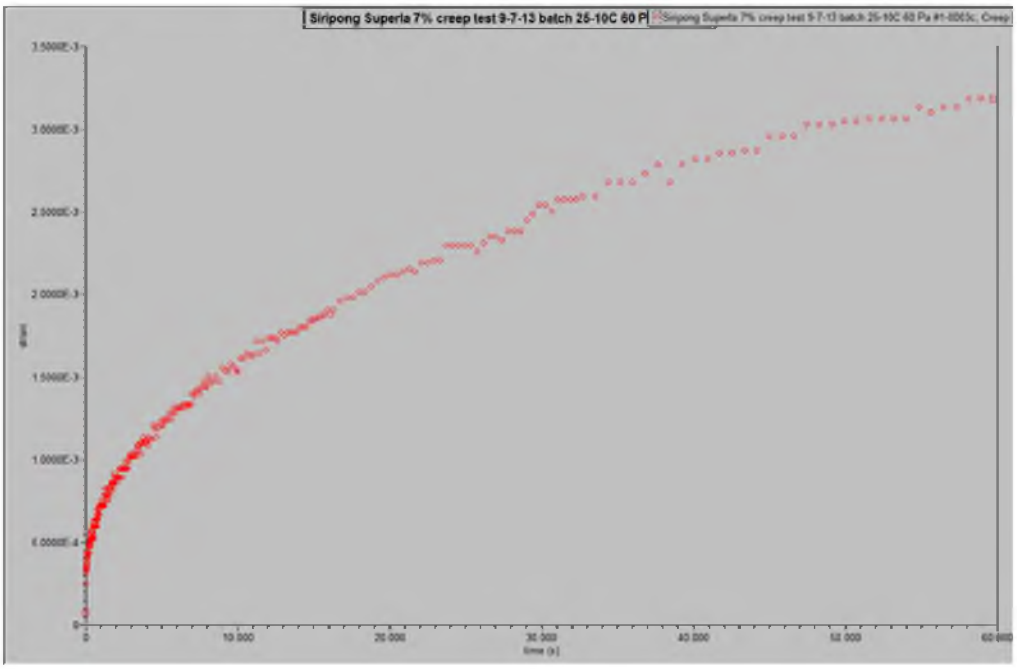

Figure 4.36. Creep test at 60 Pa. Gel condition: static cooling from 25 to 10 °C without oscillation, 0.3 °C per minute.

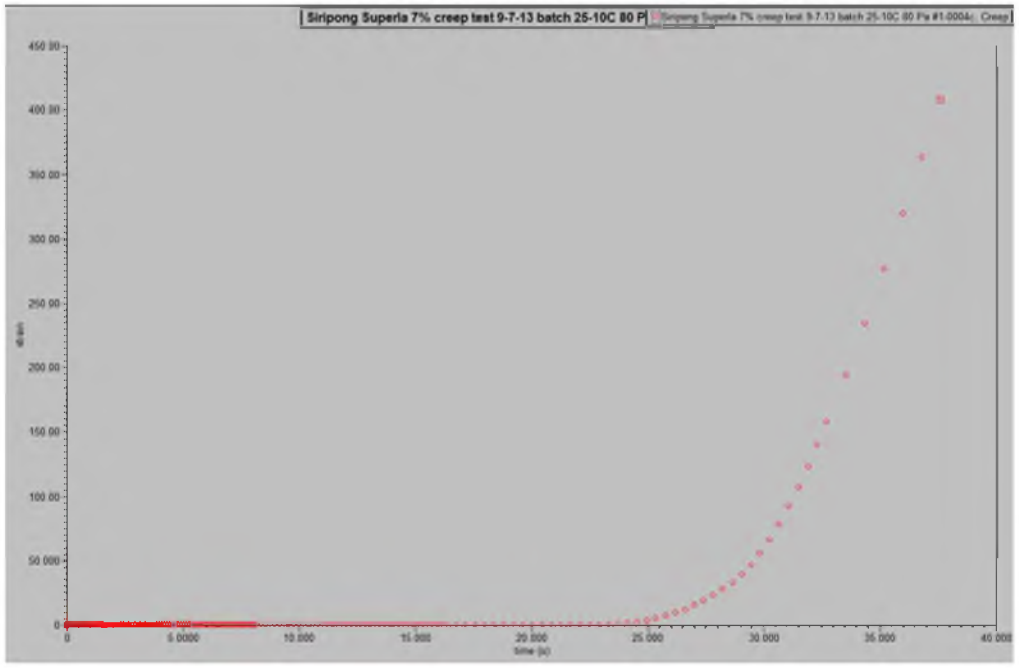

Figure 4.37. Creep test at 80 Pa. Gel condition: static cooling from 25 to 10 °C without oscillation, 0.3 °C per minute.

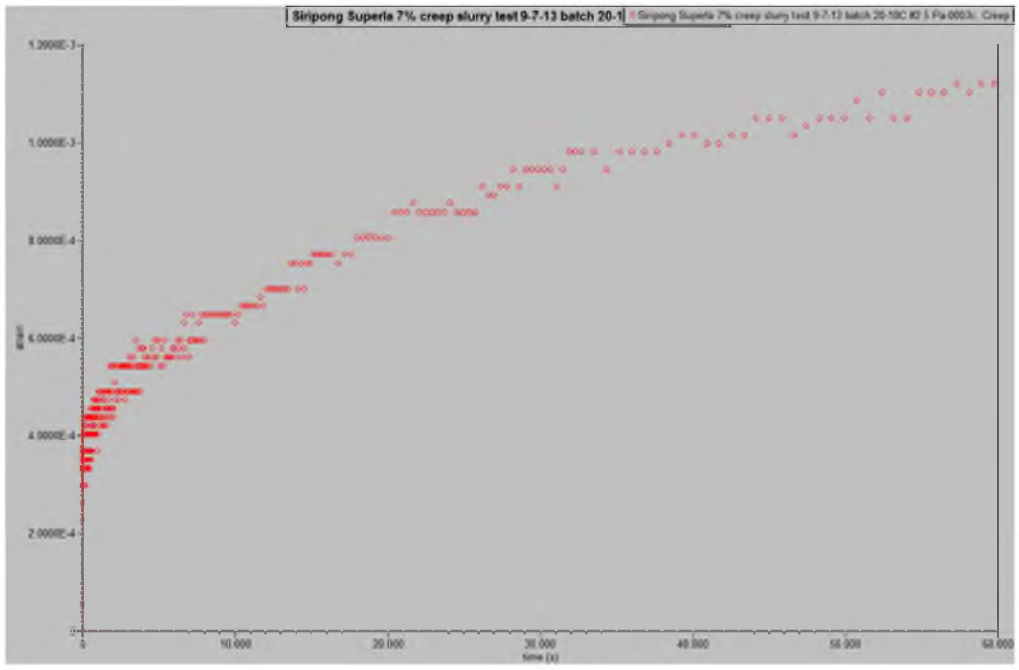

Figure 4.38. Creep test at 5 Pa. Gel condition: static cooling from 20 to 10 °C without oscillation, 0.3 °C per minute.

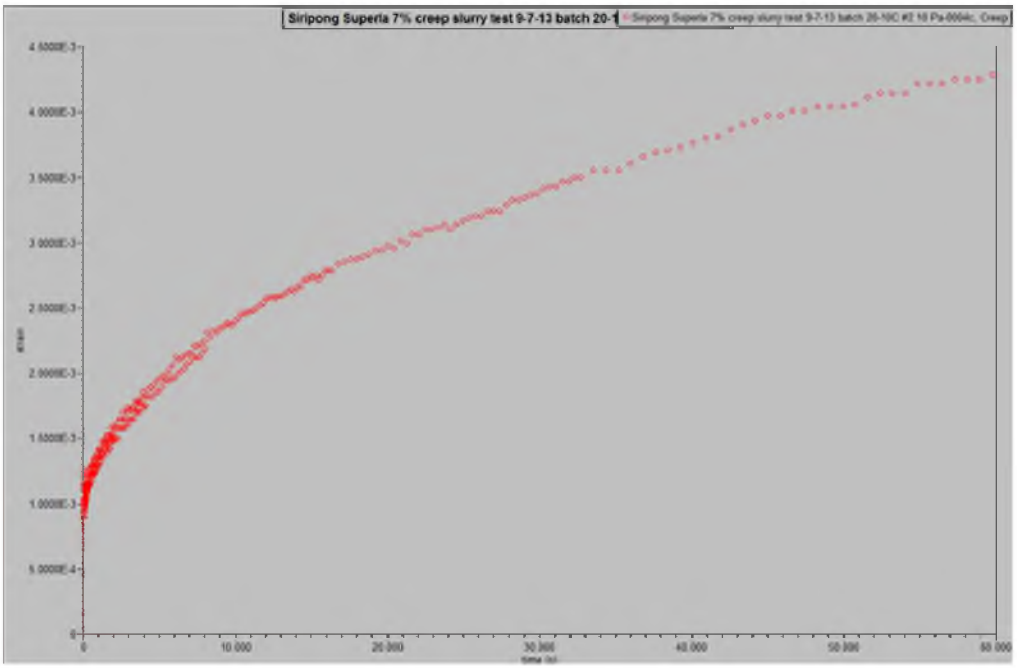

Figure 4.39. Creep test at 10 Pa. Gel condition: static cooling from 20 to 10 °C without oscillation, 0.3 °C per minute.

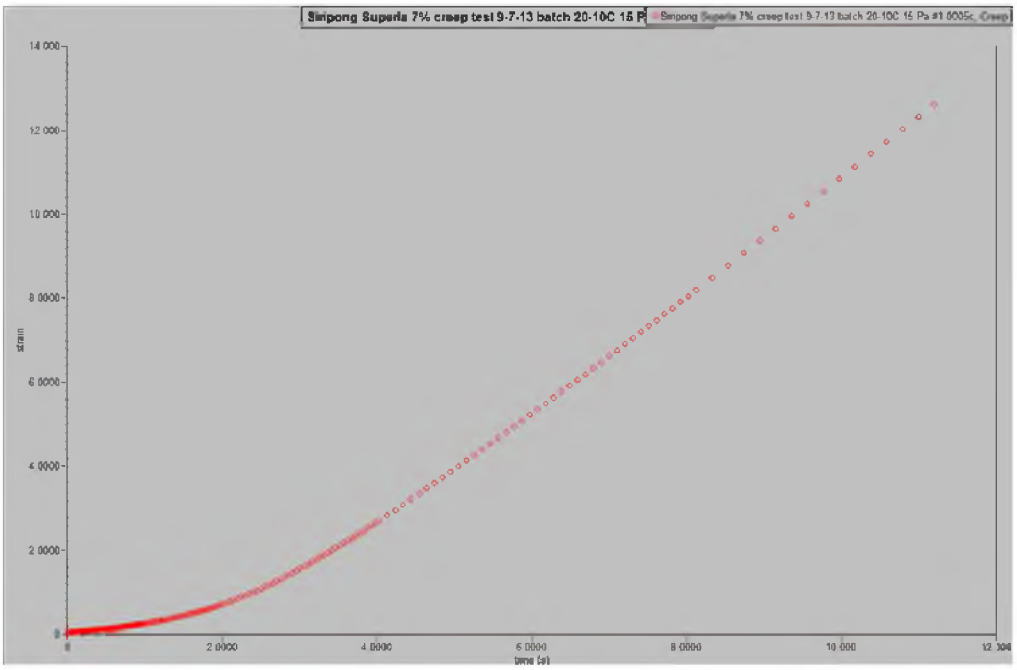

Figure 4.40. Creep test at 15 Pa. Gel condition: static cooling from 20 to 10 °C without oscillation, 0.3 °C per minute.

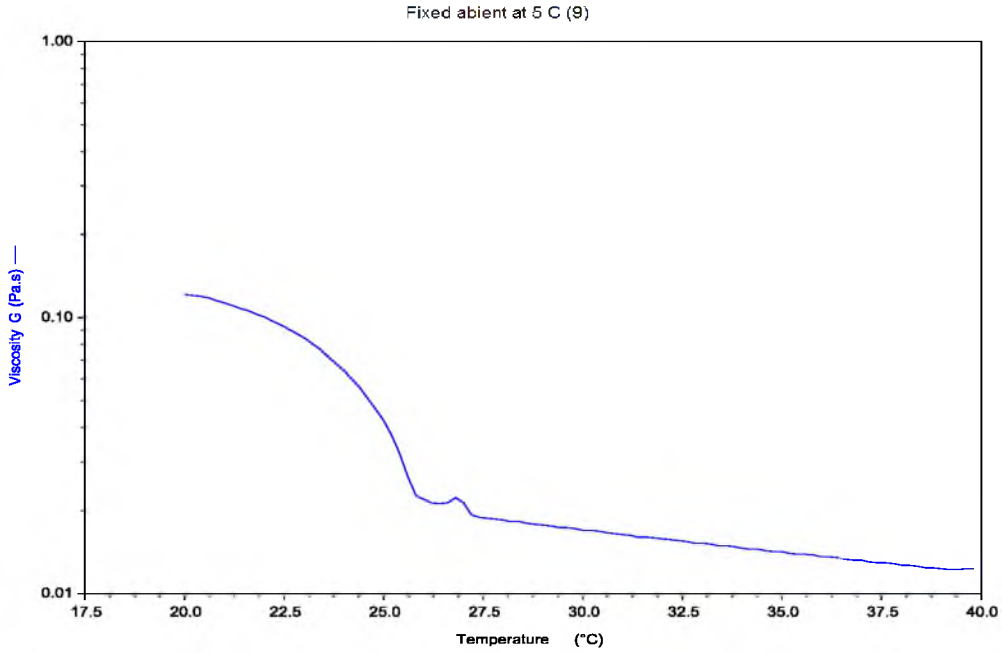

Figure 4.41. Flow test from 40-20 °C. 0.3 °C per minute, shearing rate 30 s^{-1}.

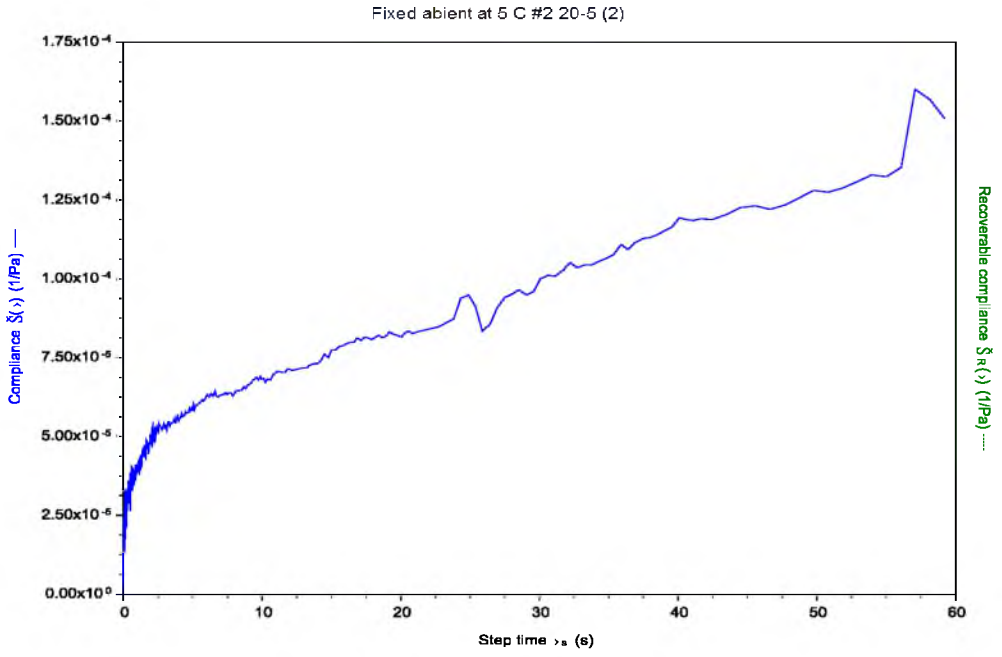

Figure 4.42. Creep test at 5 Pa. Gel condition: static cooling from 20 to 5 °C without oscillation, 0.3 °C per minute.

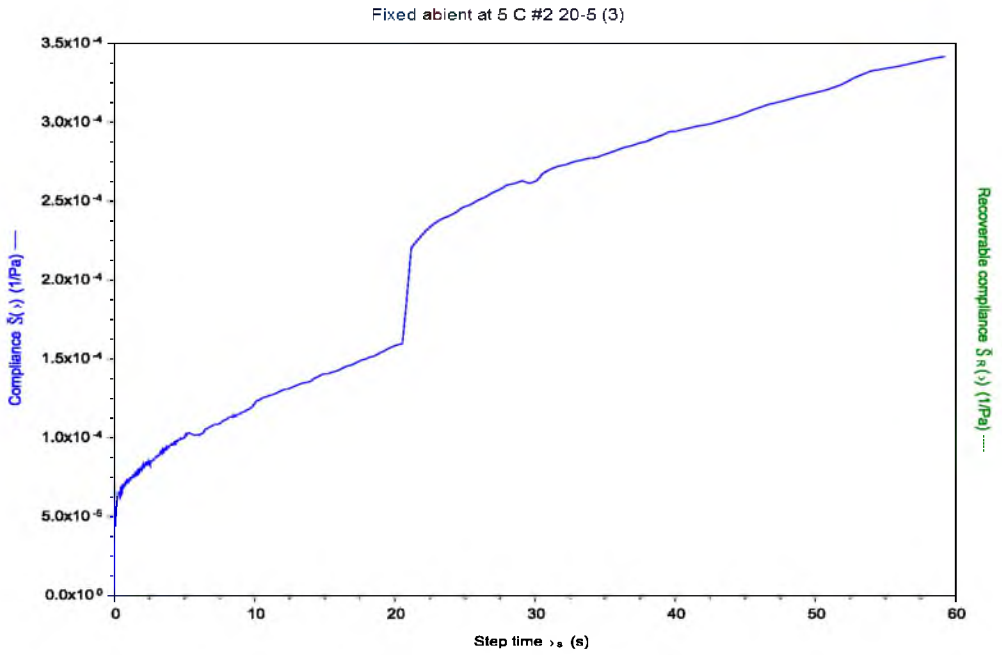

Figure 4.43. Creep test at 10 Pa. Gel condition: static cooling from 20 to 5 °C without oscillation, 0.3 °C per minute.

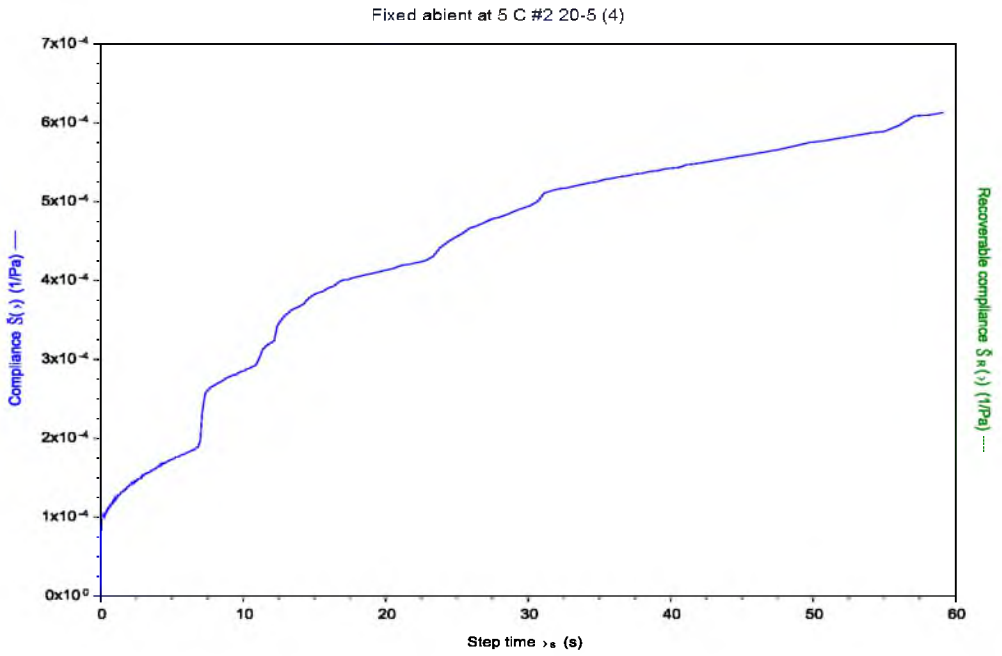

Figure 4.44. Creep test at 15 Pa. Gel condition: static cooling from 20 to 5 °C without oscillation, 0.3 °C per minute.

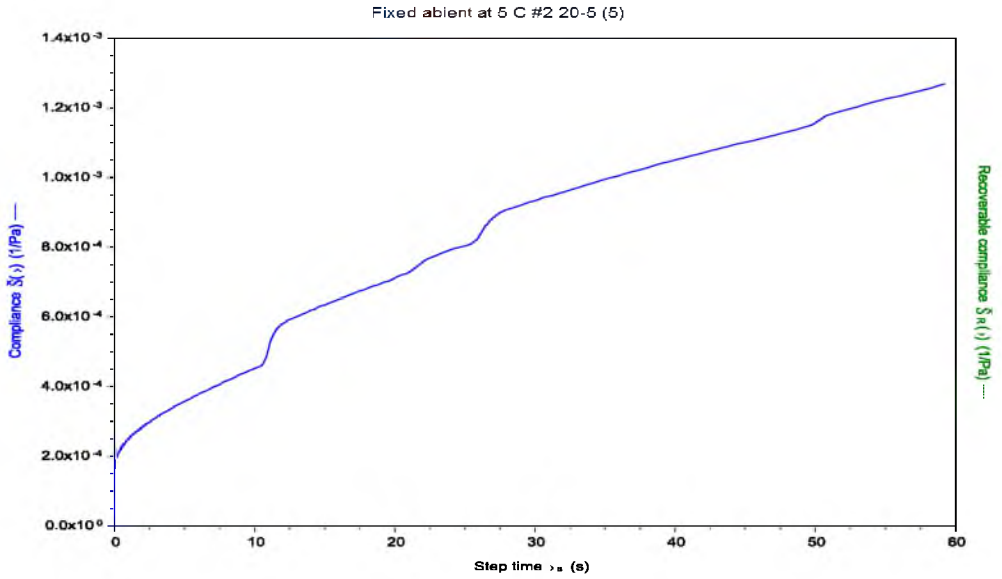

Figure 4.45. Creep test at 20 Pa. Gel condition: static cooling from 20 to 5 °C without oscillation, 0.3 °C per minute.

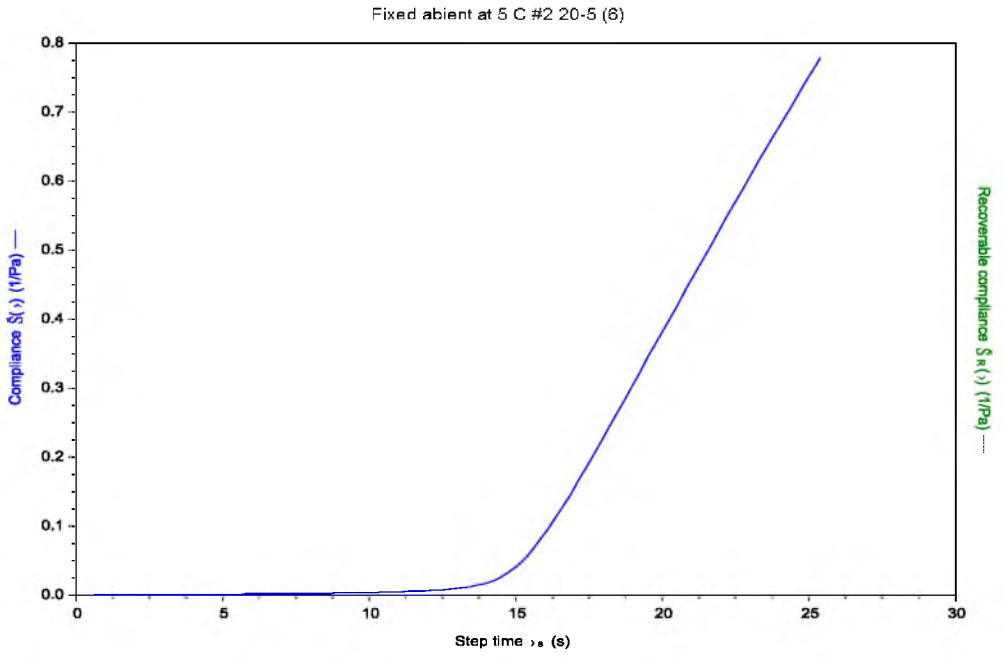

Figure 4.46. Creep test at 25 Pa. Gel condition: static cooling from 20 to 5 °C without oscillation, 0.3 °C per minute.

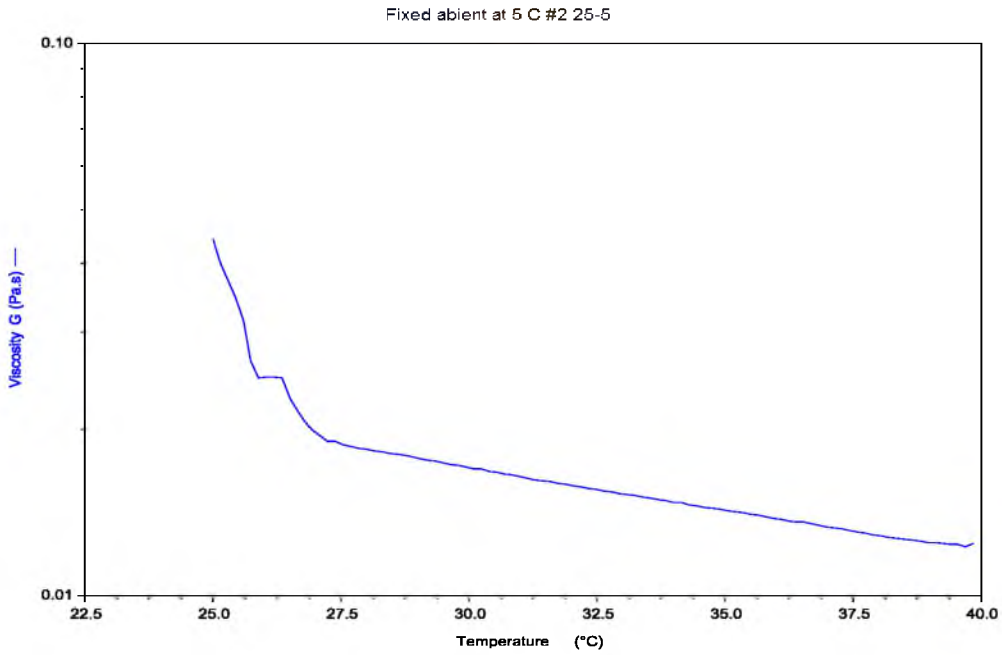

Figure 4.47. Run number 2. Flow test from 40-25 °C. 0.3 °C per minute, shearing rate 30 s^{-1}.

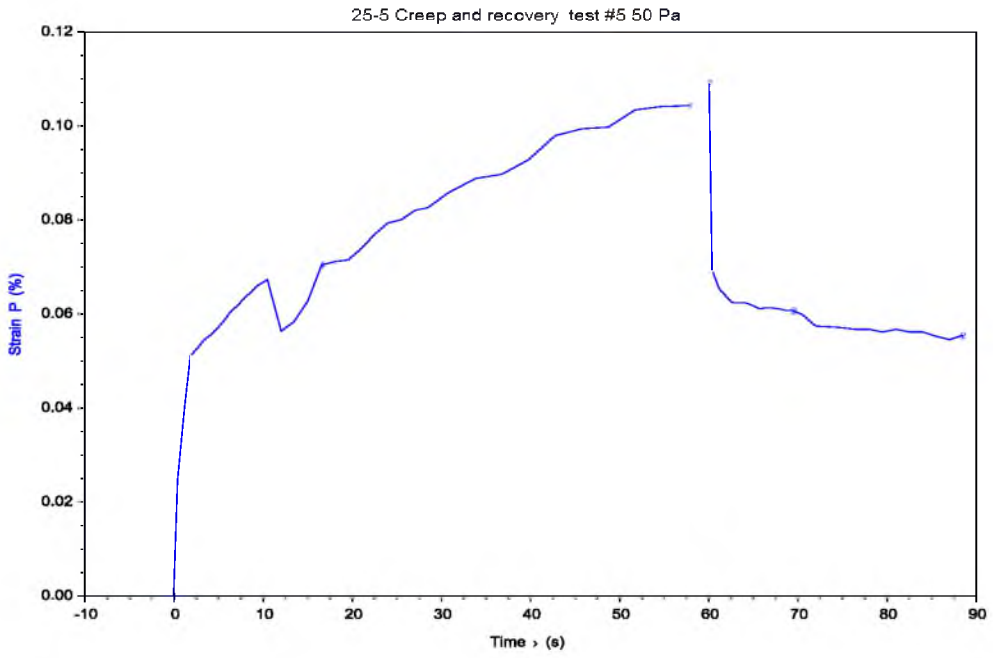

Figure 4.48. Creep and recovery test at 50 Pa. Gel condition: static cooling from 25 to 5 °C, 0.3 °C per minute.

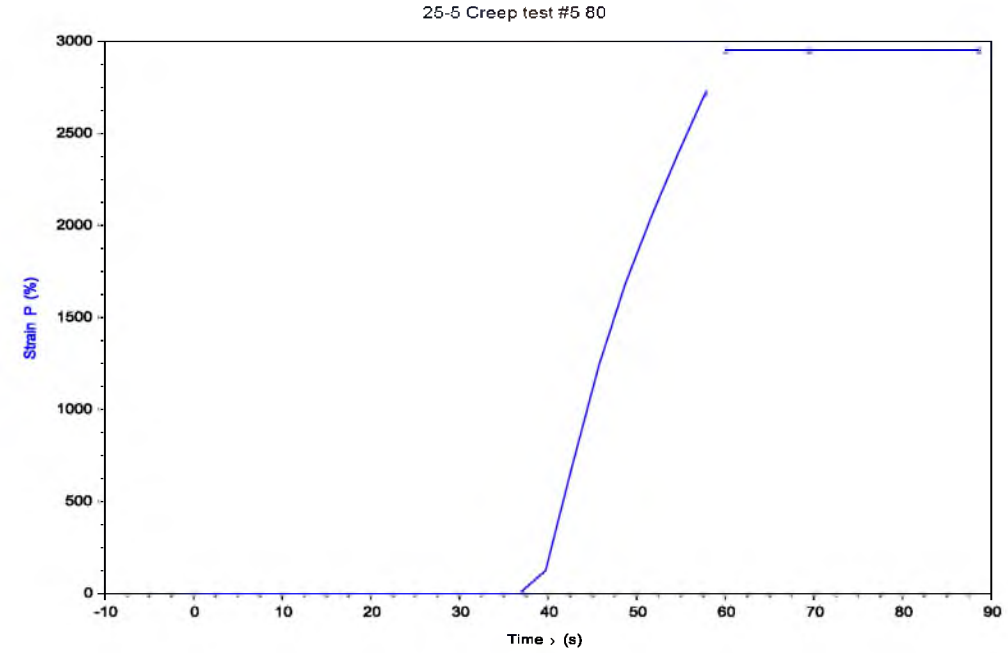

Figure 4.49. Creep test at 80 Pa. Gel condition: static cooling from 25 to 5 °C, 0.3 °C per minute.

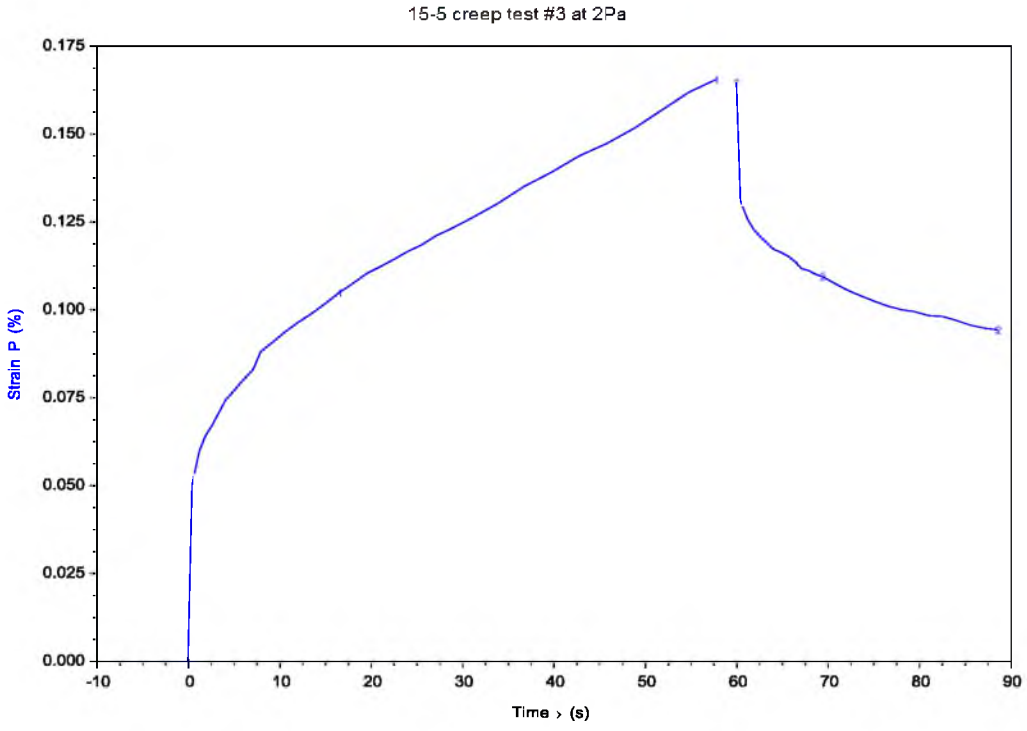

Figure 4.50. Creep and recovery test at 2 Pa. Gel condition: static cooling from 15 to 5 °C without oscillation, 0.3 °C per minute.

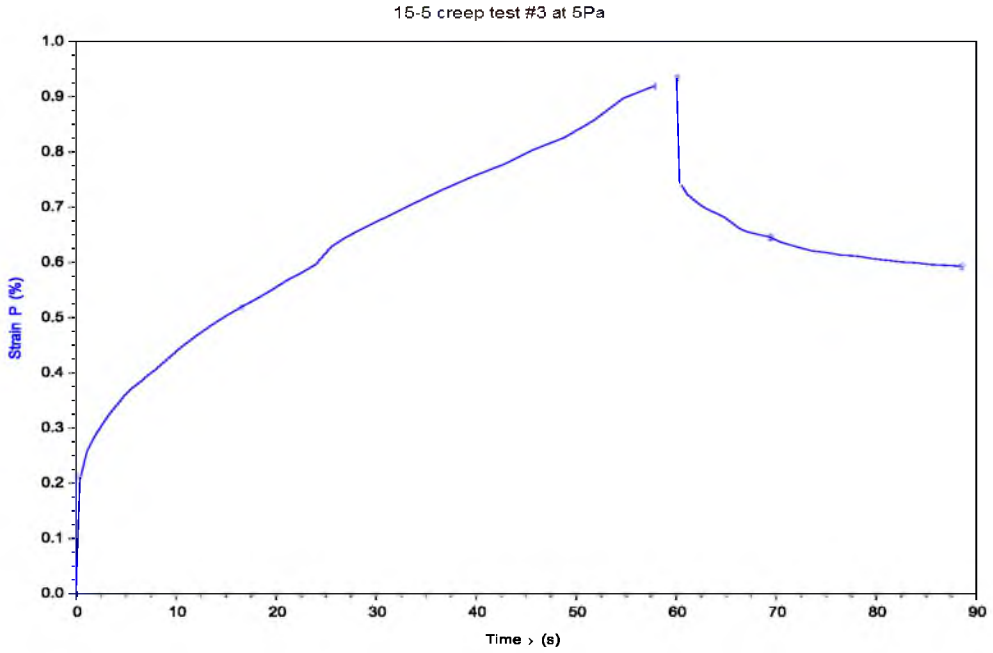

Figure 4.51. Creep and recovery test at 5 Pa. Gel condition: static cooling from 15 to 5 °C without oscillation, 0.3 °C per minute.

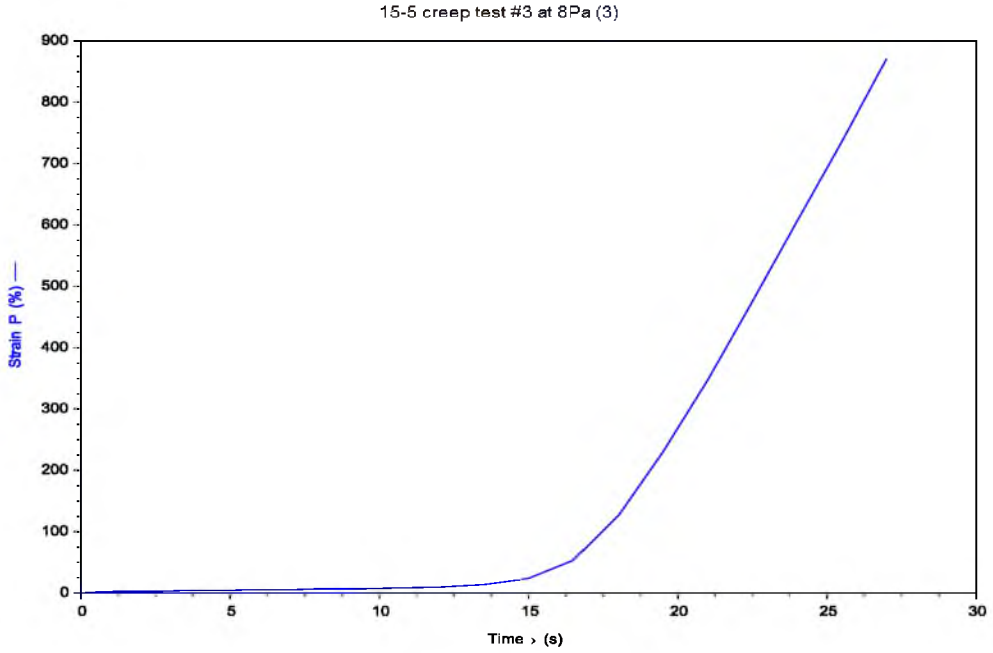

Figure 4.52. Creep at 8 Pa. Gel condition: static cooling from 15 to 5 °C without oscillation, 0.3 °C per minute.

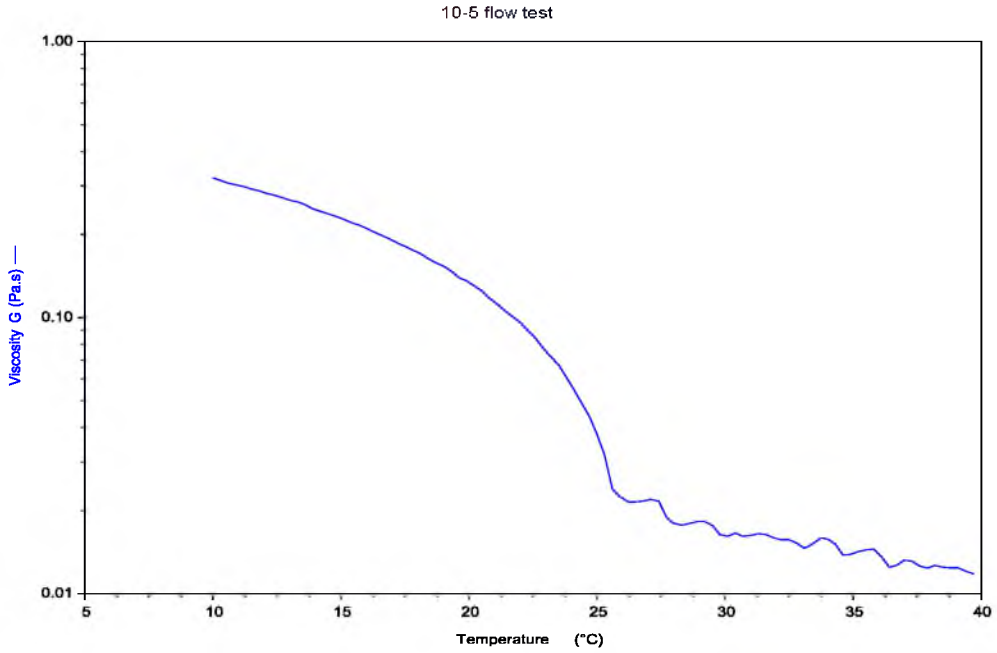

Figure 4.53. Flow test from 40 to 10 °C, 0.3 °C per minute, shearing rate 30 s^{-1}

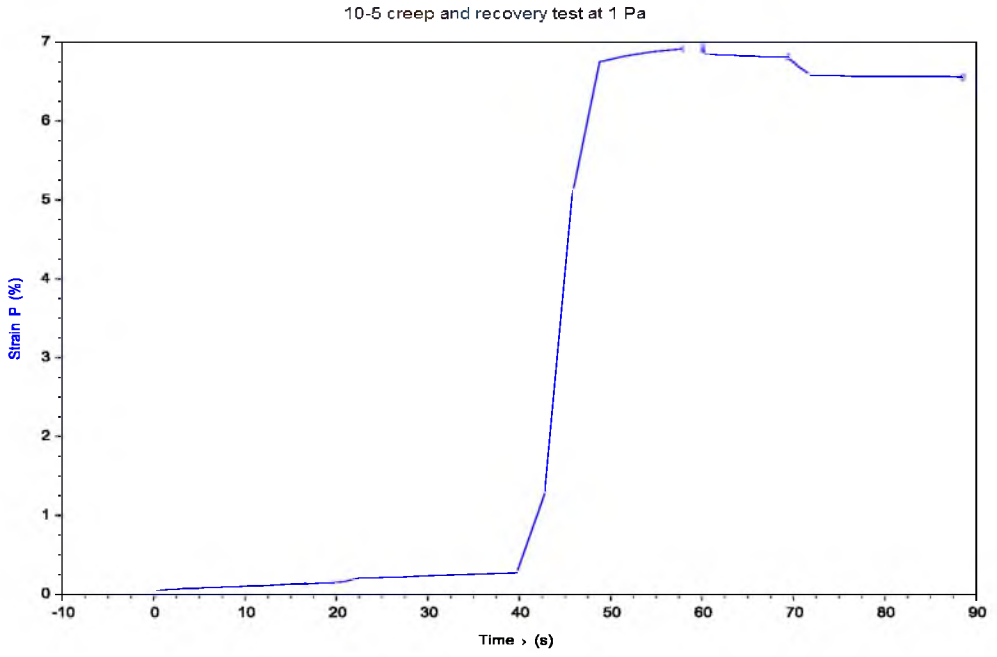

Figure 4.54. Creep and recovery test at 1 Pa. Gel condition: static cooling from 10 to 5 °C without oscillation, 0.3 °C per minute.

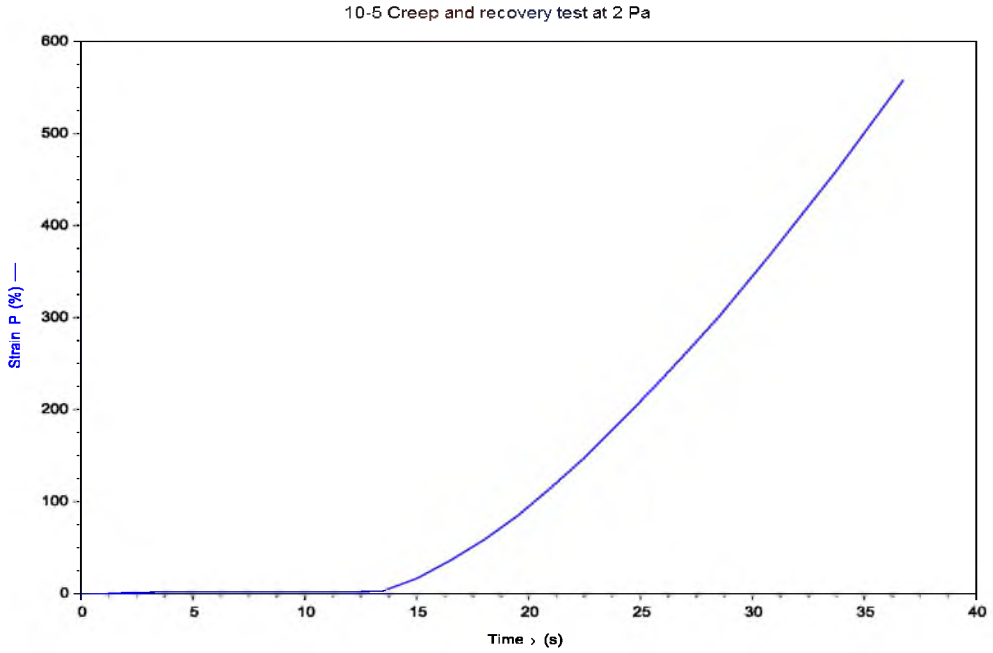

Figure 4.55. Creep at 2 Pa. Gel condition: static cooling from 10 to 5 °C without oscillation, 0.3 °C per minute.

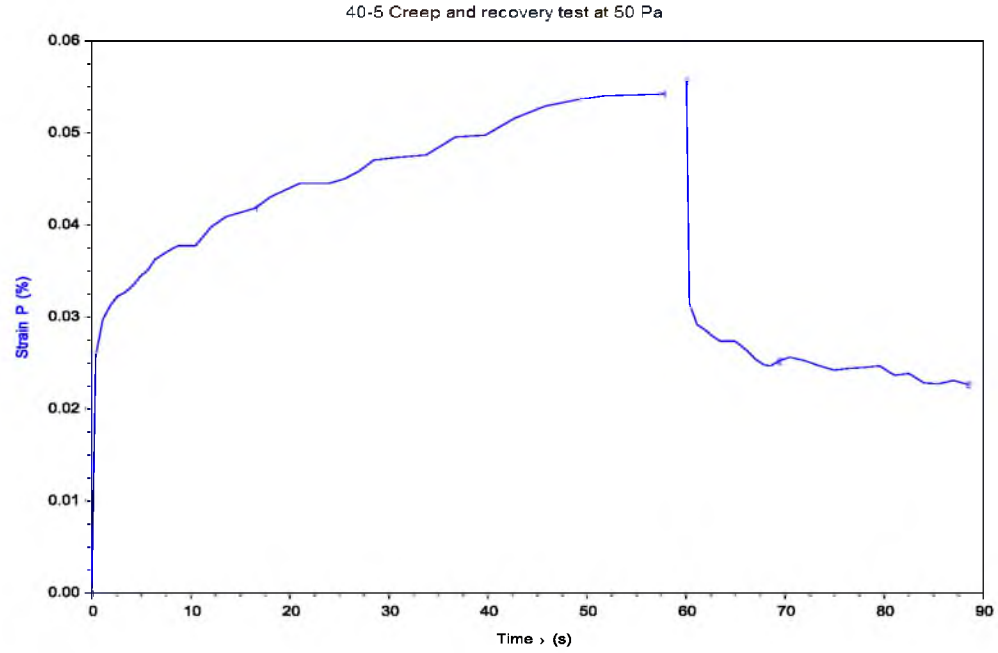

Figure 4.56. Creep and recovery test at 50 Pa. Hot flow restart from 40 to 5 °C, 0.3 °C per minute.

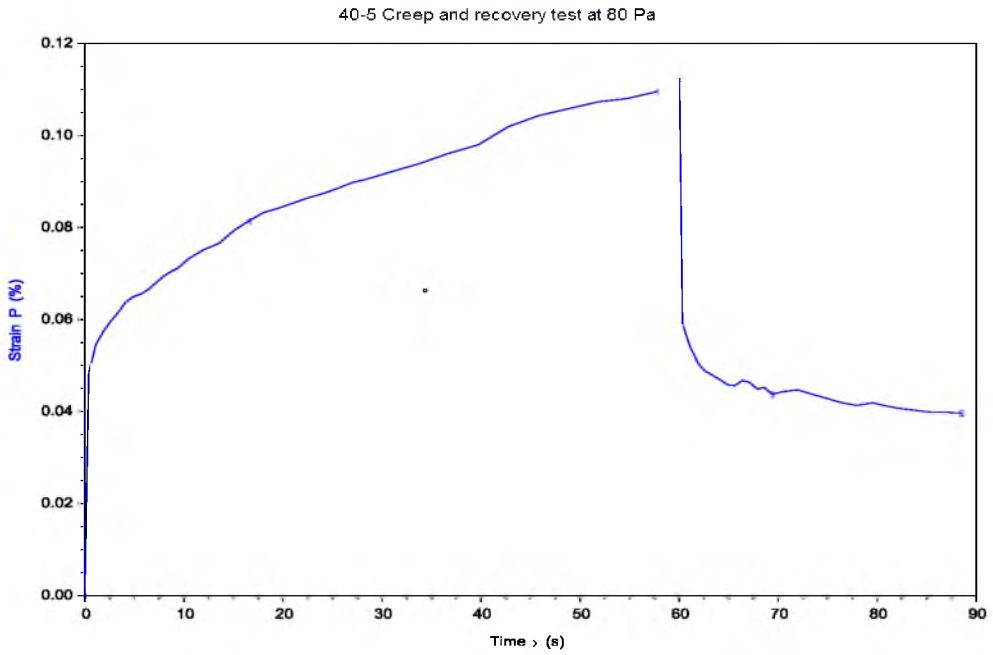

Figure 4.57. Creep and recovery test at 80 Pa. Hot flow restart from 40 to 5 °C, 0.3 °C per minute.

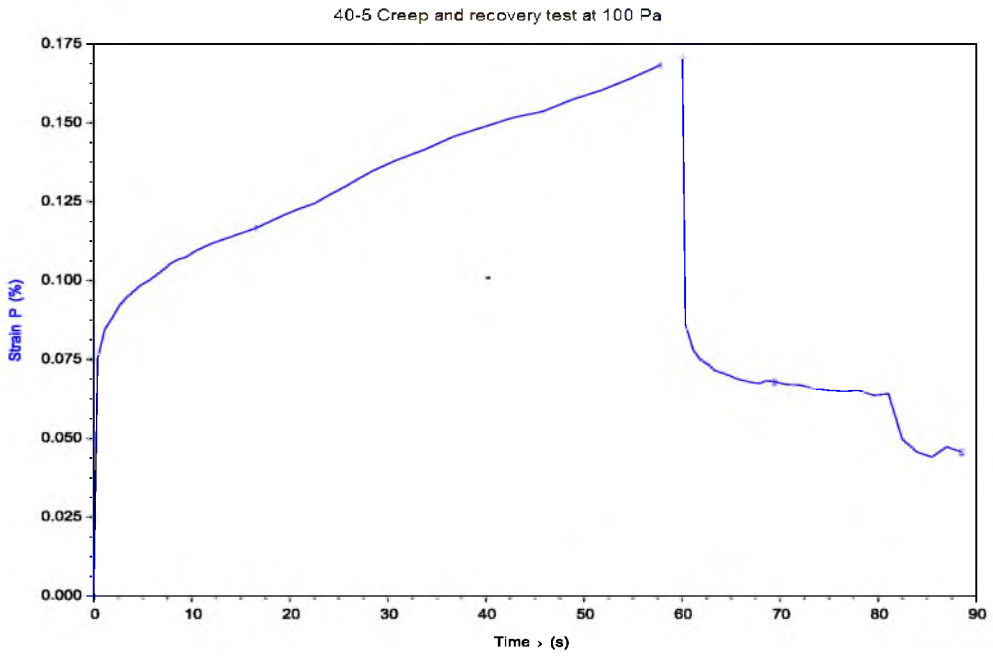

Figure 4.58. Creep and recovery test at 100 Pa. Hot flow restart from 40 to 5 °C, 0.3 °C per minute.

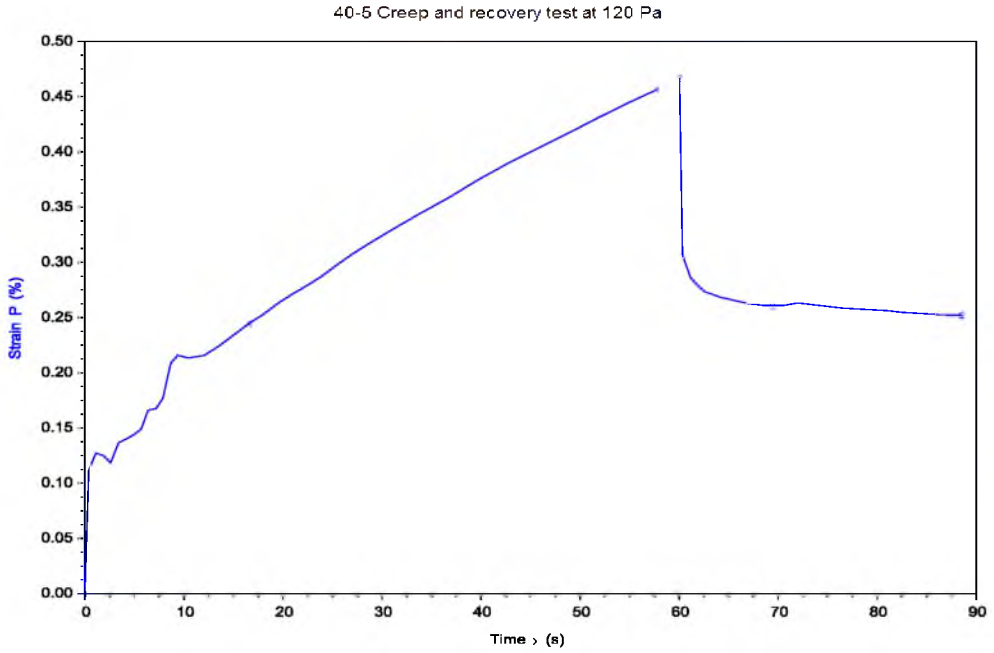

Figure 4.59. Creep and recovery test at 120 Pa. Hot flow restart from 40 to 5 °C, 0.3 °C per minute.

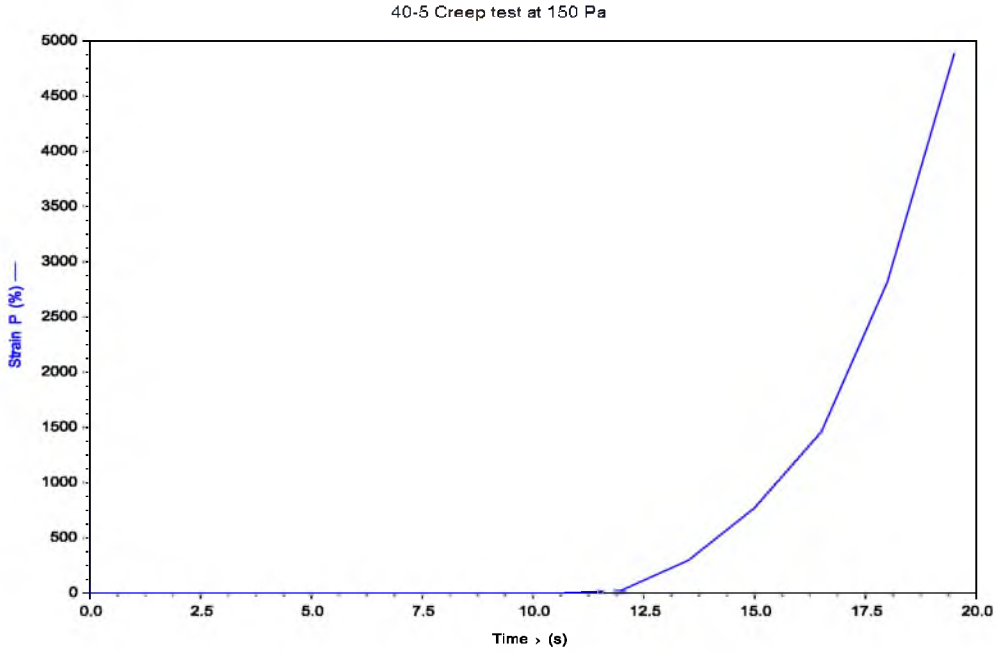

Figure 4.60. Creep at 150 Pa. Hot flow restart from 40 to 5 °C, 0.3 °C per minute.

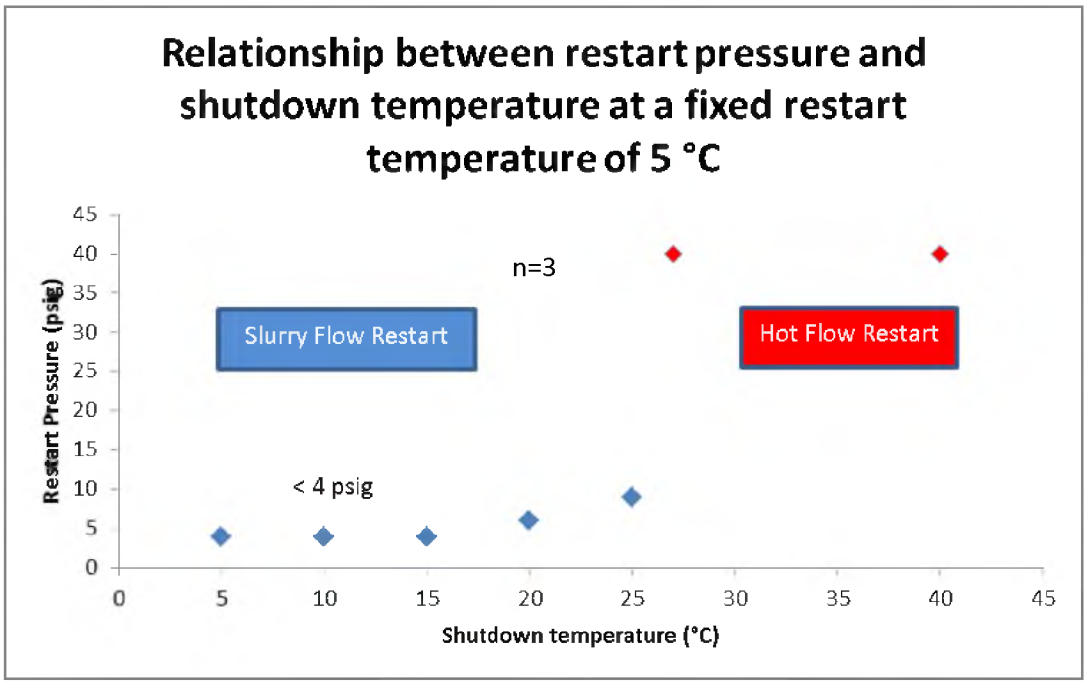

Figure 4.61. Summary of relationship between restart pressure and shutdown temperature at a fixed restart temperature of 5 °C.

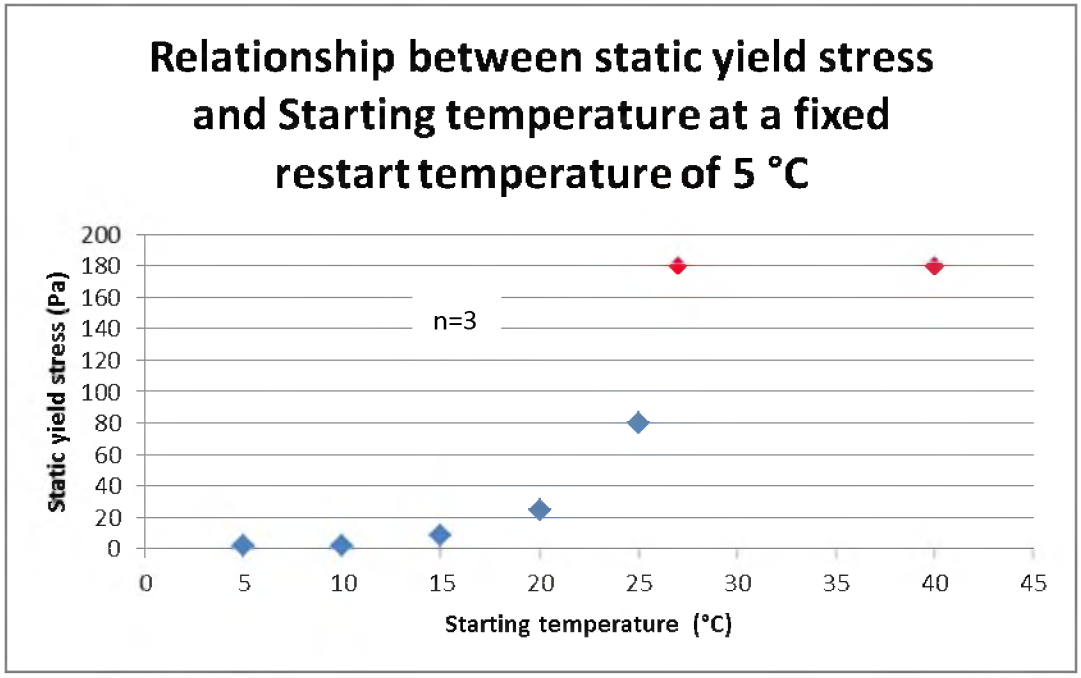

Figure 4.62. Summary of relationship between static yield stress and starting temperature at a fixed restart temperature of 5 °C.

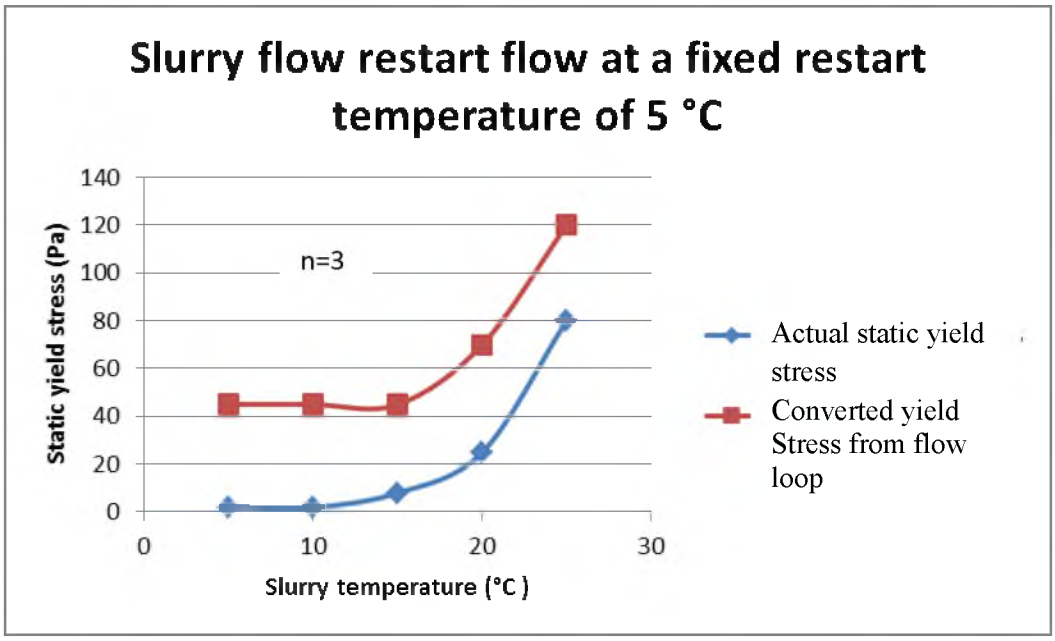

Figure 4.63. Comparison between actual yield stress measured from rheometer and predicted yield stress converted from breaking pressure data.

Table 4.1. Breaking pressure summary of slurry flow restart at a fixed ambient temperature of 0 °C

	Restart Pressure at 0 °C (psig)				
Condition/Experiment	**25-0 °C**	**20-0 °C**	**15-0 °C**	**10-0 °C**	**5-0 °C**
#1	16.6-20.5	4.1-6.4	4-8.1	N/A	N/A
#2	16.6-20.1	4.1-7.7	< 3.9	N/A	N/A
#3	8.1-12.4	5.9-8.2	< 3.9	N/A	N/A
Average	12.4-20.5	4.1-8	< 4	< 4	< 4

* The gel formed at 10 °C and 5 °C would have likely broken at an upstream pressure lower than 4 psig

Table 4.2. Breaking pressure summary of slurry flow restart at a fixed ambient temperature of 5 °C

	Restart Pressure at 5 °C (psig)				
Condition/Experiment	**25-5 °C**	**20-5 °C**	**15-5 °C**	**10-5 °C**	**5-5 °C**
#1	5.5-7.8	< 3.9	< 3.8	N/A	N/A
#2	5.7-8.1	4-6.2	< 4.4	N/A	N/A
#3	8.1-10.2	3.9-5.5	N/A	N/A	N/A
Average	6.5-8.7	3.9-6	< 4	< 4	< 4

* The gel formed at 10 °C and 5 °C would have likely broken at an upstream pressure lower than 4 psig

Table 4.3. Breaking pressure summary of slurry flow restart at a fixed ambient temperature of 10 °C

	Restart Pressure at 10 °C (psig)			
Condition/Experiment	**25-10 °C**	**20-10 °C**	**15-10 °C**	**10-10 °C**
#1	< 4.2	< 4.6	N/A	N/A
#2	< 4.1	< 1.9	N/A	N/A
#3	< 3.9	< 4.8	N/A	N/A
Average	< 4	< 4	< 4	< 4

* The gel formed from at 15 °C and 10 °C would have likely broken at an upstream pressure lower than 4 psig

Table 4.4. Hot flow restart breaking summary

	Static cooling from 40 °C			
Cooling Condition/Experiment	**40-15 °C**	**40-12 °C**	**40-10 °C**	**40-5 °C**
#1 Breaking pressure (psig)	3.8-6.7	12.1-14.7	16.6-20.5	36-40.5
#2 Breaking pressure (psig)	4.1-7.2	12.9-14.5	15.2-20.1	36.2-40.5
#3 Breaking pressure (psig)	5.4-6.3	N/A	15.7-20.2	36.5-40.2
#4 Breaking pressure (psig)	N/A	N/A	15.6-20.5	38.1-39.9

Table 4.5. Hot flow and slurry restart at a fixed temperature of 5 °C

Yield Stress (Pa)						
Condition/Number	**40-5 °C**	**27-5 °C**	**25-5 °C**	**20-5 °C**	**15-5 °C**	**10-5 °C**
#1	80-150	100-150	80-120	15-20	5-8	1-2
#2	120-150	120-150	50-80	20-25	2-4	1-2
#3	150-180	120-150	50-60	22-25	4-8	1-2
Predict	120-180	120-150	50-80	15-25	4-8	1-2

Table 4.6. Correlation between flow loop and rheometer at a restart temperature of 5 °C

Condition	40-5 °C	27-5 °C	25-5 °C	20-5 °C	15-5 °C	10-5 °C	5 °C
Restart pressure from the flow loop (psig)	36-40.5	36-40.5	6-10.2	3.9-6.2	< 4	< 4	< 4
Converted to τ_S (Pa)	400-450	400-450	70-120	45-70	< 45	< 45	< 45
τ_S from rheometer (Pa)	120-180	120-180	50-80	15-25	5-8	1-2	< 1

Table 4.7. Correlation between flow loop and rheometer at a restart temperature of 10 °C

Condition	40-10 °C	30-10 °C	25-10 °C	20-10 °C
Restart pressure from the flow loop (psig)	15.5-20.5	15.5-20.5	< 4	< 4
Converted to τ_S (Pa)	175-230	175-230	< 45	< 45
τ_S from rheometer (Pa)	80-120	80-120	60-80	10-15

CHAPTER 5

CONCLUSION

5.1 Summary

5.1.1 First version of flow loop

The results showed that restart temperature affects how strong a gel is. Changing the restart temperature between 10 °C, 12 °C, and 15 °C affects the restart pressure. The results showed that the gel was weakest at 15 °C and broke at a restart pressure of 20 psig. Cold flow is one method to solve waxes depositing inside the pipelines, and it works very well compared to other methods. A cold flow restart temperature of 15 °C required a breaking pressure of approximately10 psig instead of 20 psig for the hot flow case. Because cold flow allows for lower restart pressures after shutdown, oil companies can reduce initial pipeline costs or maintenance costs by using lower quality pipelines. Another significant result was that upstream pressure applied during the cooling period did not affect the strength of the waxy gels.

5.1.2 Second version of flow loop

The results showed that the second version of the flow loop was more suited to make slurry compared to the first version because the scraped heat exchanger was used to remove wax deposition while circulating the waxy oil. Slurry restart and hot flow restart methods were compared at three different fixed restart temperatures (0, 5, 10 °C). Higher

restart temperatures resulted in a decrease of the strength of the gel which meant the breaking pressure was less than at lower restart temperature. At a fixed ambient temperature of 5 °C, hot flow restart had a breaking pressure between 36-40 psig while slurry flow restart greatly dropped in all cases. For example, at a slurry temperature of 25 °C, the restart pressure was between 6 and 12 psig which was 25% of the strength of the hot flow case. The breaking pressure even decreased for a slurry temperature of 20 °C. In this case, the breaking pressure was between 4 and 6 psig. Any slurry temperature below 15 °C would break after opening the downstream valve (restart pressure less than 4 psig). This result was consistent with previous research, and it could prove to be an effective method to prevent or reduce wax deposition in the pipeline.

5.1.3 Rheology

A Discovery HR and an AR 500 rheometer were used to measure the WAT, gelation temperature, elastic yield stress and static yield stress. The results show that the WAT was fixed around 26-27 °C for every condition, but the gelation temperature changed when the testing conditions were varied. The elastic yield stress zone was determined by a creep test in which the gel crept and partially recovered. Gelled oil breaks when the applied stress exceeds the static yield stress. Two fixed restart temperature at 5 and 10 °C were studied for both slurry flow and hot flow restart. The results showed similarity in the flow loop. Higher restart temperatures decrease the strength of the gel which meant that the breaking pressure was less than at lower restart temperatures. For instance, in the hot flow case, the static yield stress was between 120 and 180 Pa for a restart temperature of 5 °C while it was between 80 and 100 Pa for a

restart temperature of 10 °C. One interesting thing was that there was no difference in yield stress value for starting temperatures above WAT.

At a fixed ambient temperature of 5 °C, hot flow restart had a yield stress between 120-180 Pa while slurry flow restart greatly dropped in all cases. For example, at a slurry temperature of 25 °C, the yield stress was between 50 and 60 Pa, which was half of the hot case yield stress. The stress even decreased as the slurry temperature decrease from 20 to 15 to 10 °C. These yield stresses were between 15-25 Pa, 5-8 Pa, and 1-2 Pa respectively.

5.1.4 Correlation between the second version of flow loop and rheology

Finally, the main point of this research is to compare a slurry restart between the flow loop and rheometer. The predicted yield stress found using the flow loop pressure measurement and equation 1 and 2 was over predicted in most condition (See Tables 8 and 9 to compare the results). A fixed temperature of 5 °C was primarily used in order to find a relationship between the flow loop and rheology. It seems like the difference of yield stress between the flow loop and rheometer was larger for the hot flow case and higher slurry temperatures. However, the actual yield stress from the rheometer and predicted yield stress from the flow loop show similar trends. The reason that the trends look similar but the values are different could be related to effects from the flow loop such as loading rate, flow rate, shear rate from the pump and factors related to rheology such as frequency and shear rate. The slurry flow restart method can reduce the restart pressure required to break the wax deposition in the pipeline by a factor of 10 for the flow loop; slurry flow restart can decrease the static yield stress of gel by a factor of 100 for the rheometer compared to the hot flow case.

5.2 Comparison results with previous work

Most of the experiments that the author observed were in good agreement with the theoretical gelled waxy crude oil characteristics that previous researchers have found:

1. Gel is time dependent
2. Thermal driving force or temperature range affects the strength of the gel
3. The slurry method makes gel weaker than hot flow restart

However, there are a few investigations that are contrary to what it is generally observed. In some cases, the yield stress from flow loop was over predicted by the rheometer. From the author's point of view, the gel could slip between the cone and plate at high temperatures of slurry flow and hot flow restart for the rheometer. However, using the 2° cone and plate should get rid of the slipping problem. The reason for the over prediction might be related to flow loop conditions such as loading rate, flow rate and shear rate from the pump and rheology conditions such as frequency and shear rate; this most likely requires further investigation. Another possibility was that the waxy oil gel might degrade as time passed by and could affect the results.

5.3 Future work

The purpose of this research is to solve and prevent petroleum transportation problems via pipeline. The author has modified and developed the flow loop to reach the goal, which is to find the optimum conditions required to remove the waxy gel. Most of the results the author found are consistent with previous research, but some of them are different. There are still some conditions that need to be investigated.

First, shear rate between the scraped heat exchanger and rheometer needs to be the same since it could have an effect on the wax crystal size while cooling under flow

conditions. Canty vision (cross-polarized camera system) could be used to inspect the particle size of the wax crystals. Second, experiments using waxy crude oil should be performed under the same conditions as the model oil in order to make a comparison. FTIR or DSC should be used to obtain the precipitation curve of the oil used. A solubility curve can also be obtained from FTIR or DSC. Finally, it might prove useful to make slurry using the flow loop and then extract the sample to put in the rheometer, and then statically cool to the restart temperature. This way, the compositions of the slurry used in both types of tests are the same.

The author thinks that this research is going in the right direction, and it has almost reached the point where petroleum companies can use this method to remove waxy gelled deposits in the pipeline. This project will be beneficial to others in the future, especially for businesses that work on the transportation of petroleum and chemical fluids. The use of cold flow would save costs on materials and provide an efficient procedure to restart gelled waxy oil in a pipeline. Finally, this research will need to be added to and improved. It would be perfect if this research gets completed, so that petroleum companies will receive massive benefits related to the cutting down of costs. Finally, the implementation of cold flow might result in oil and petroleum prices dropping.

APPENDIX

RAW DATA

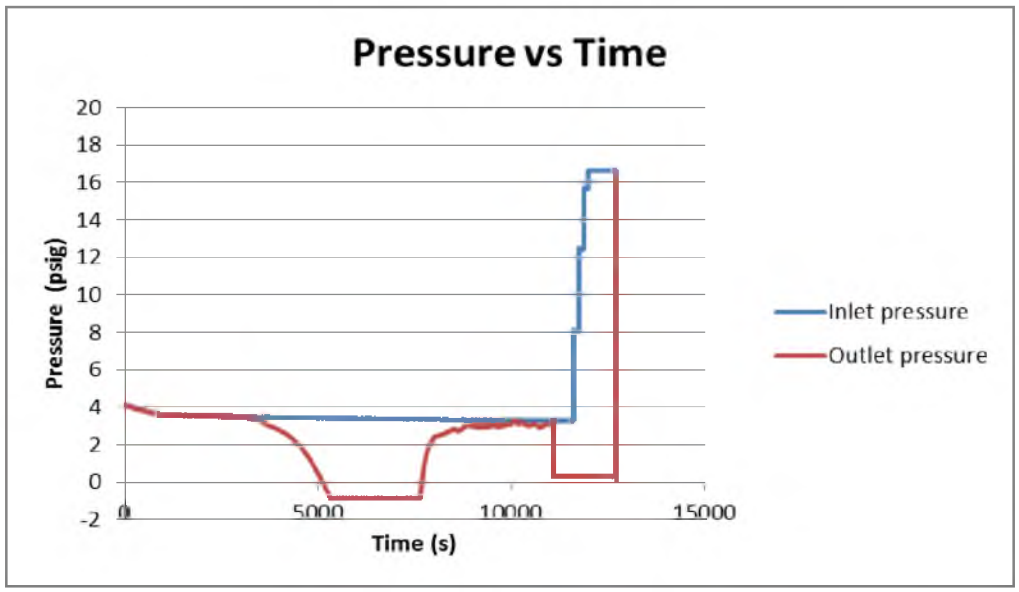

Figure A.1. Run number 2. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36.2 and 40.5 psig (measured by manually observing a pressure gauge).

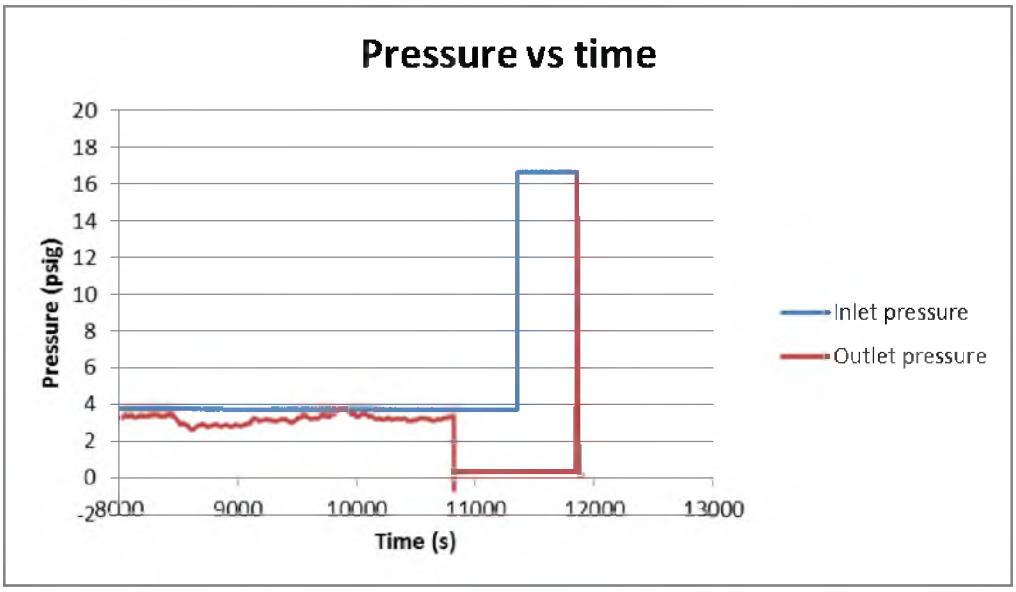

Figure A.2. Run number 3. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36.5 and 40.2 psig (measured by manually observing a pressure gauge).

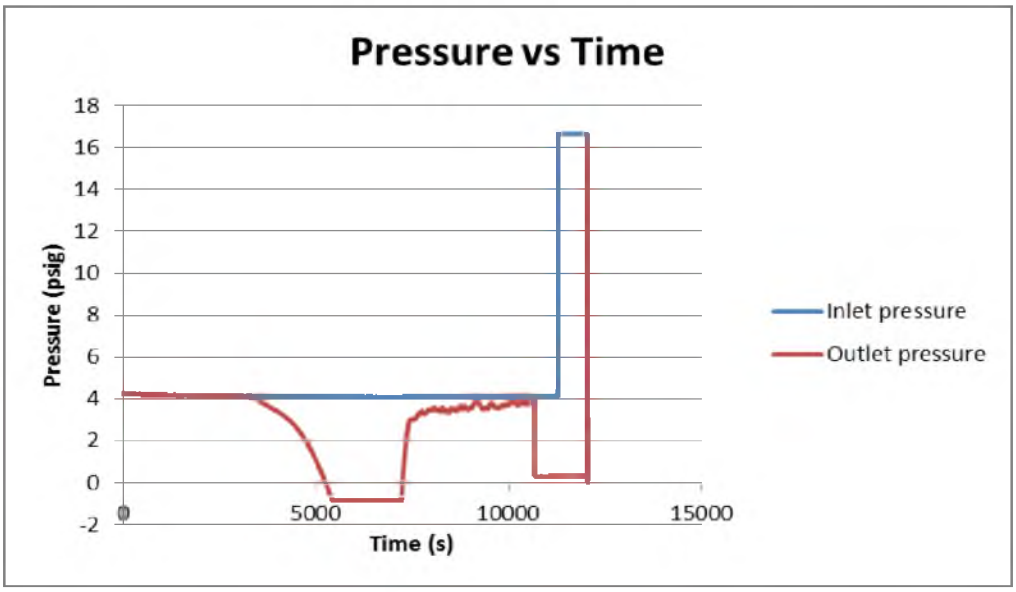

Figure A.3. Run number 4. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 38.1 and 39.9 psig (measured by manually observing a pressure gauge).

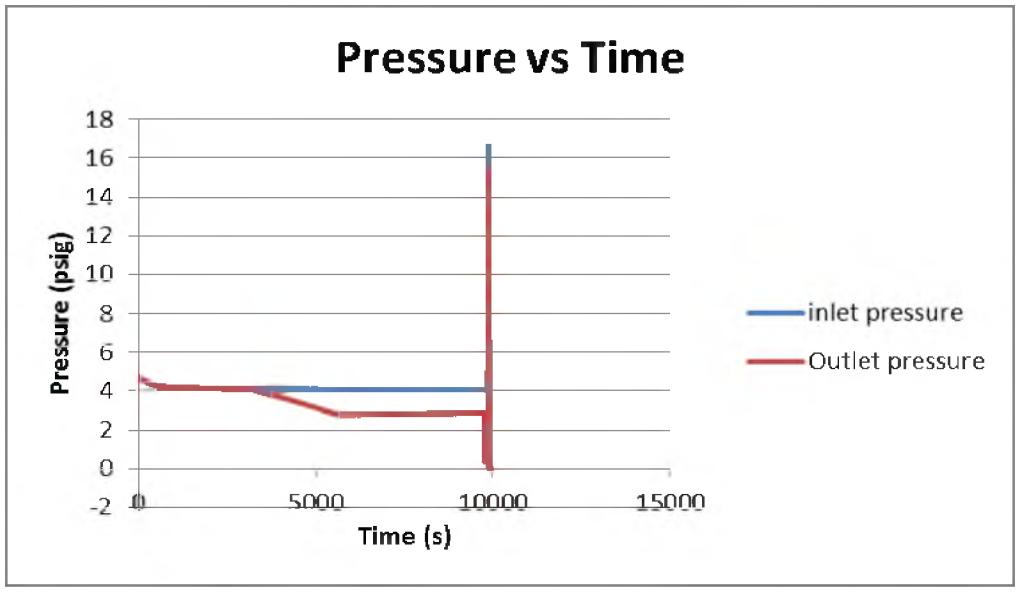

Figure A.4. Run number 1. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 16.6 and 20.5 psig (measured by manually observing a pressure gauge).

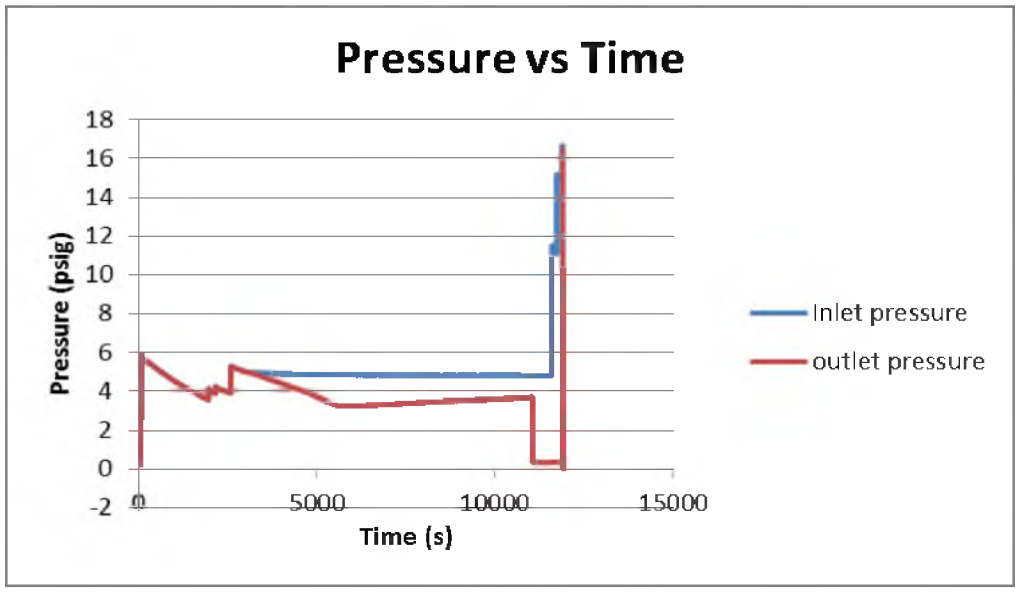

Figure A.5. Run number 2. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 15.5 and 20.1 psig (measured by manually observing a pressure gauge).

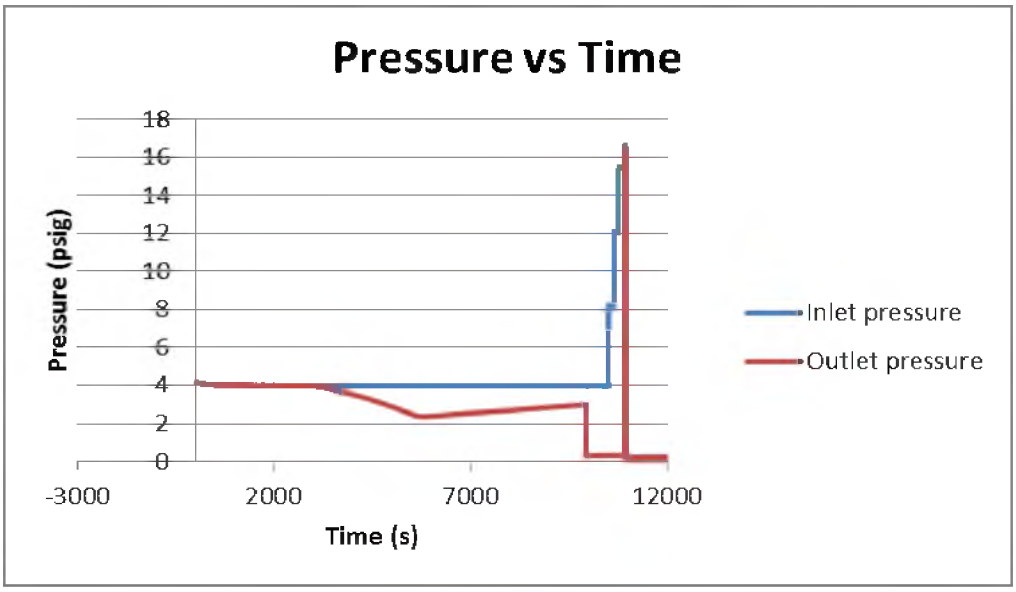

Figure A.6. Run number 3. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 15.7 and 20.2 psig (measured by manually observing a pressure gauge).

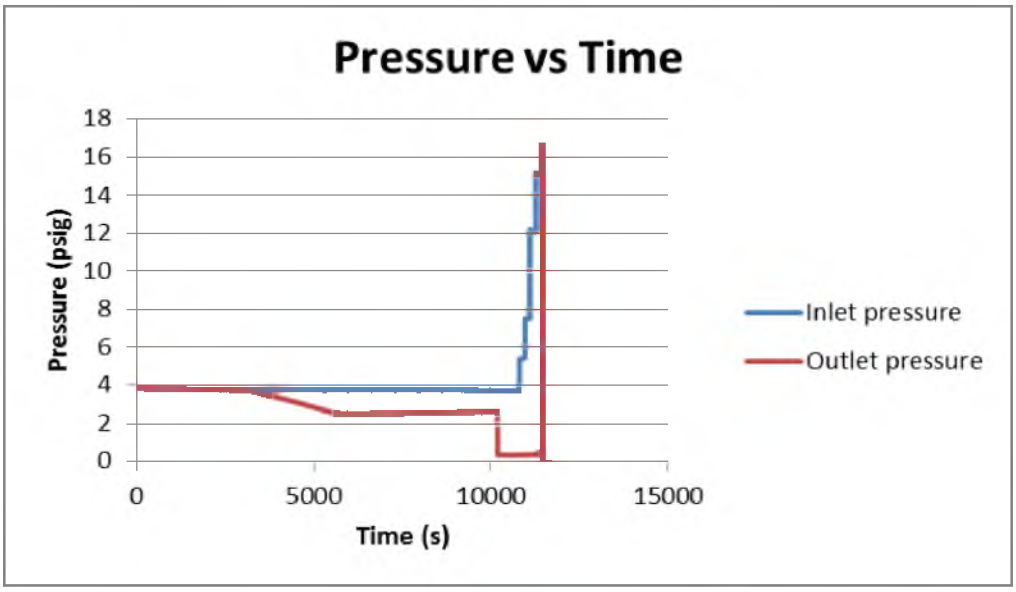

Figure A.7. Run number 4. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 15.6 and 20.5 psig (measured by manually observing a pressure gauge).

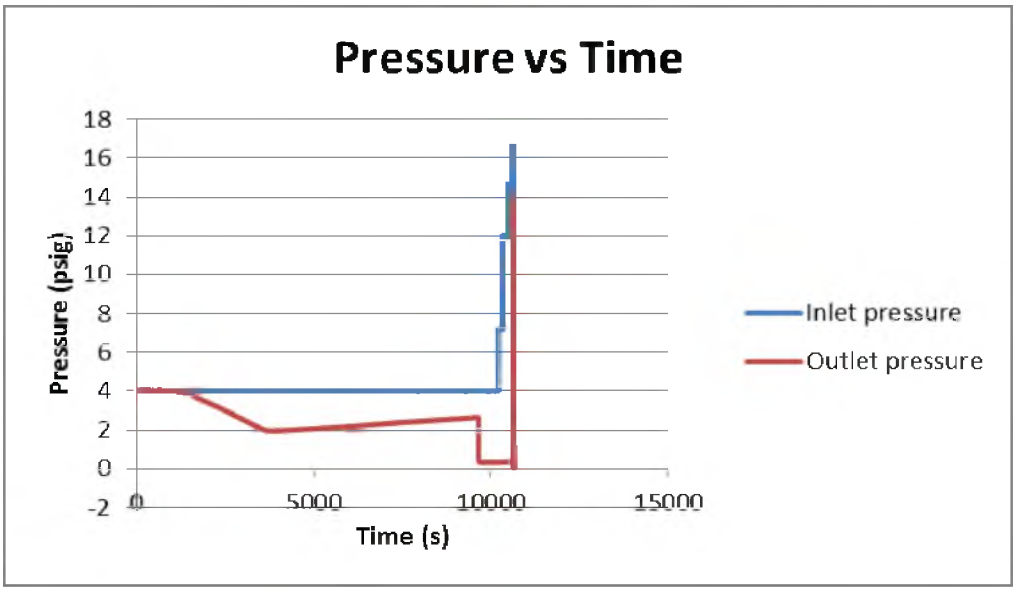

Figure A.8. Run number 1. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 15.5 and 20.2 psig (measured by manually observing a pressure gauge).

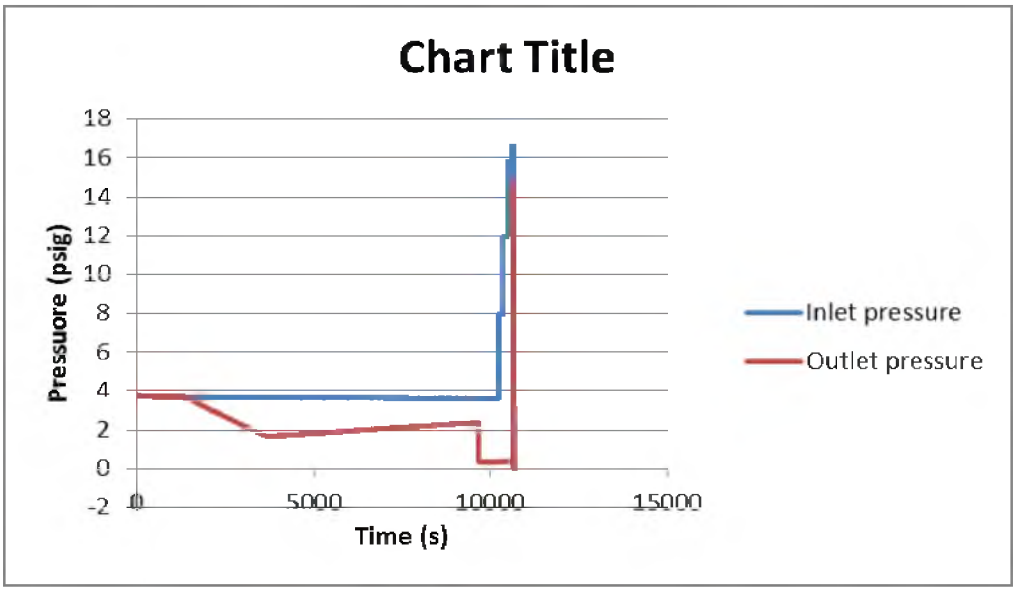

Figure A.9. Run number 2. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 10 °C (0.3 °C per minute). *The gel broke between 15.9 and 20.3 psig (measured by manually observing a pressure gauge).

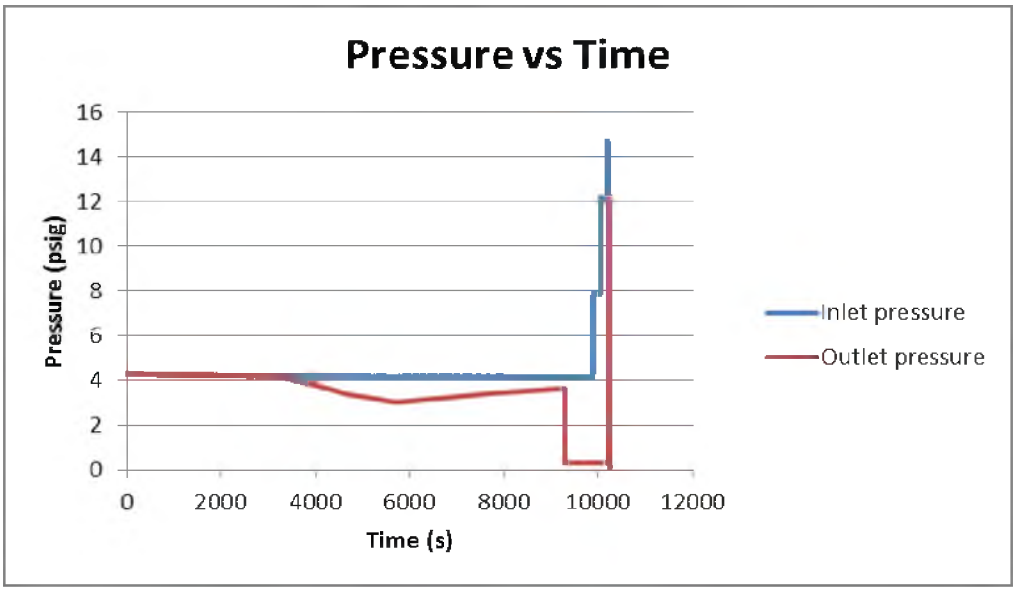

Figure A.10. Run number 1. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 12 °C (0.3 °C per minute).

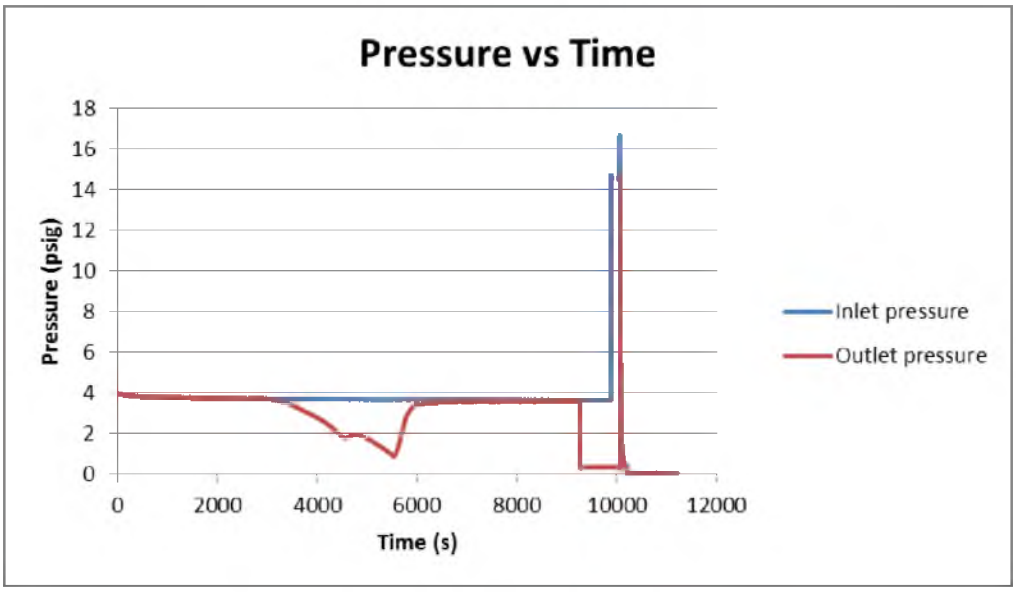

Figure A.11. Run number 2. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 12 °C (0.3 °C per minute).

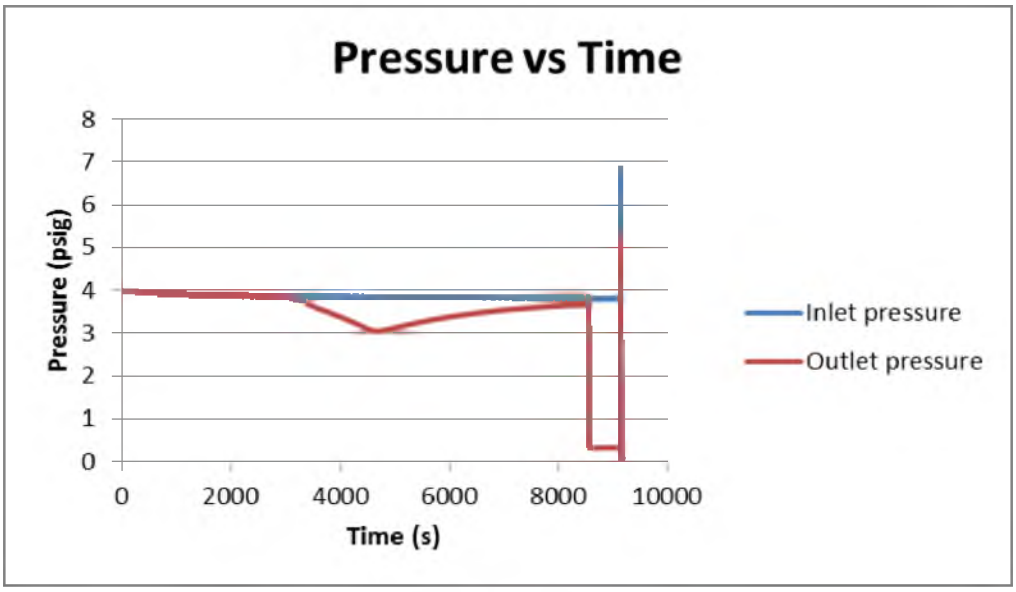

Figure A.12. Run number 2. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 15 °C (0.3 °C per minute).

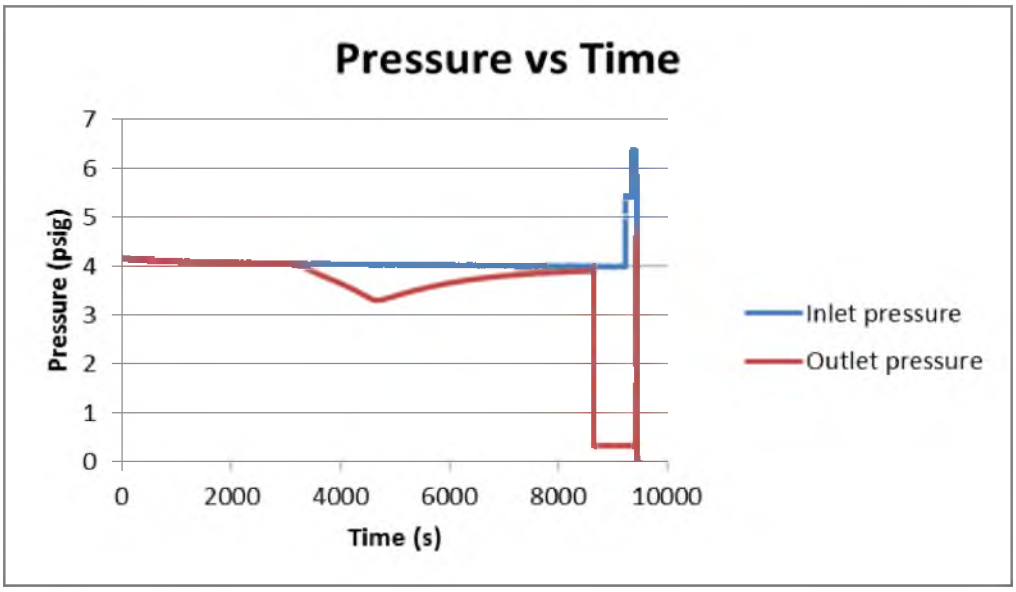

Figure A.13. Run number 3. Applied an upstream pressure of 4 psig with a hot flow condition at 40 °C and cooled down to 15 °C (0.3 °C per minute)

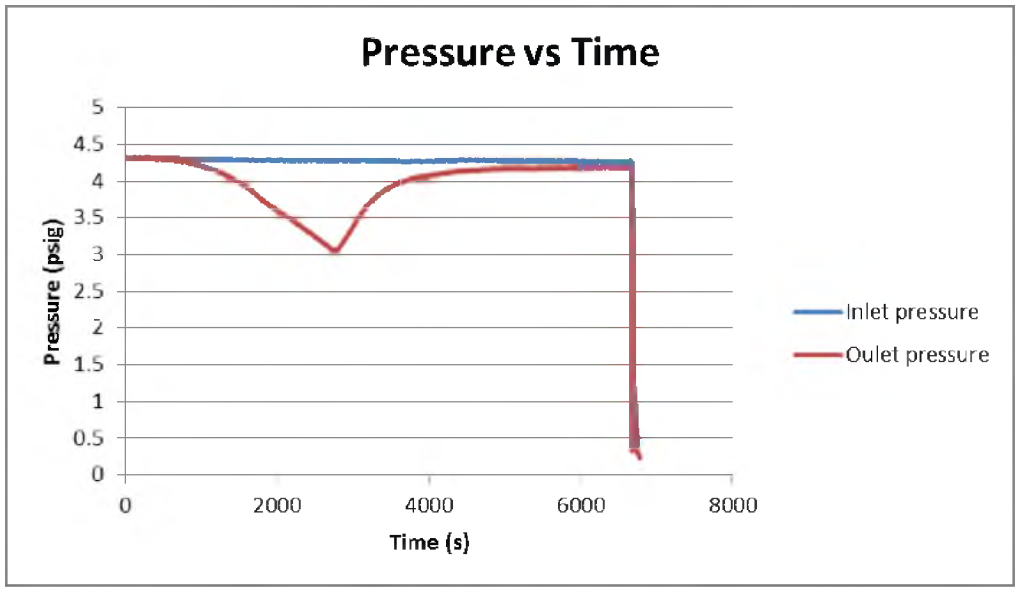

Figure A.14. Run number 2. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 10 °C (0.3 °C per minute).

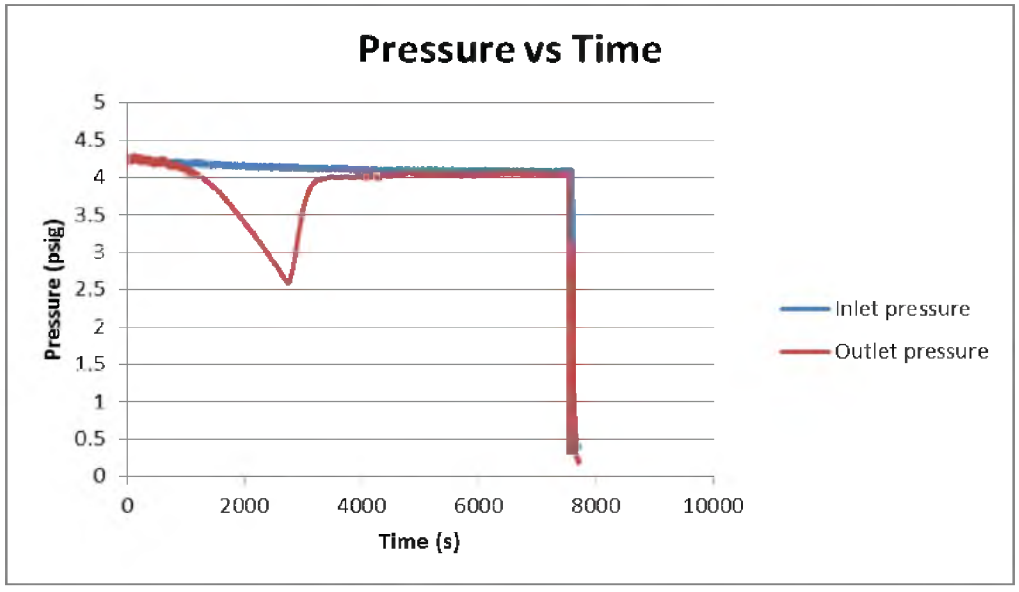

Figure A.15. Run number 3. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 10 °C (0.3 °C per minute).

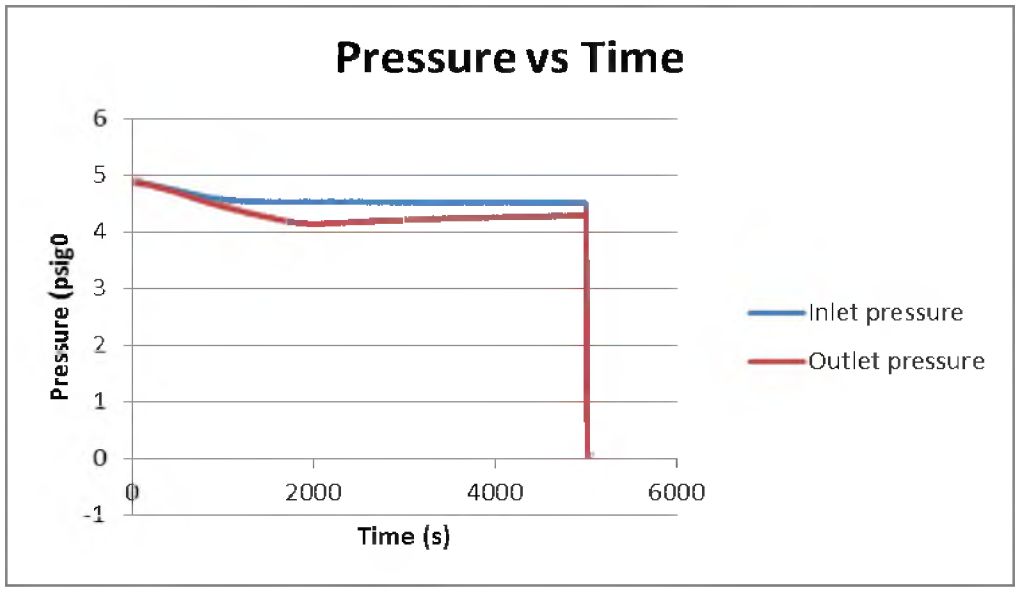

Figure A.16. Run number 1. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 10 °C (0.3 °C per minute).

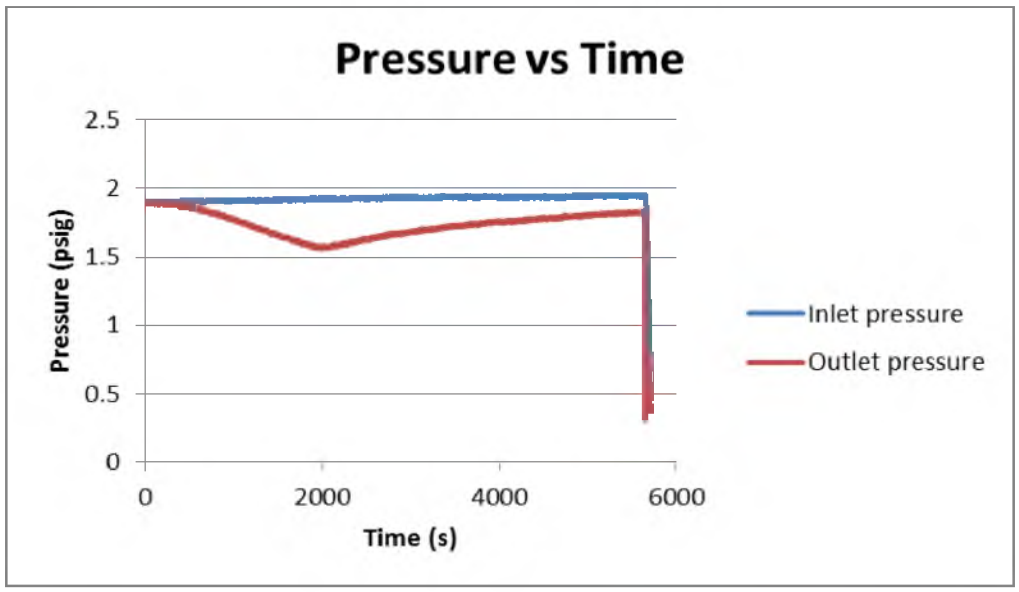

Figure A.17. Run number 2. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 10 °C (0.3 °C per minute).

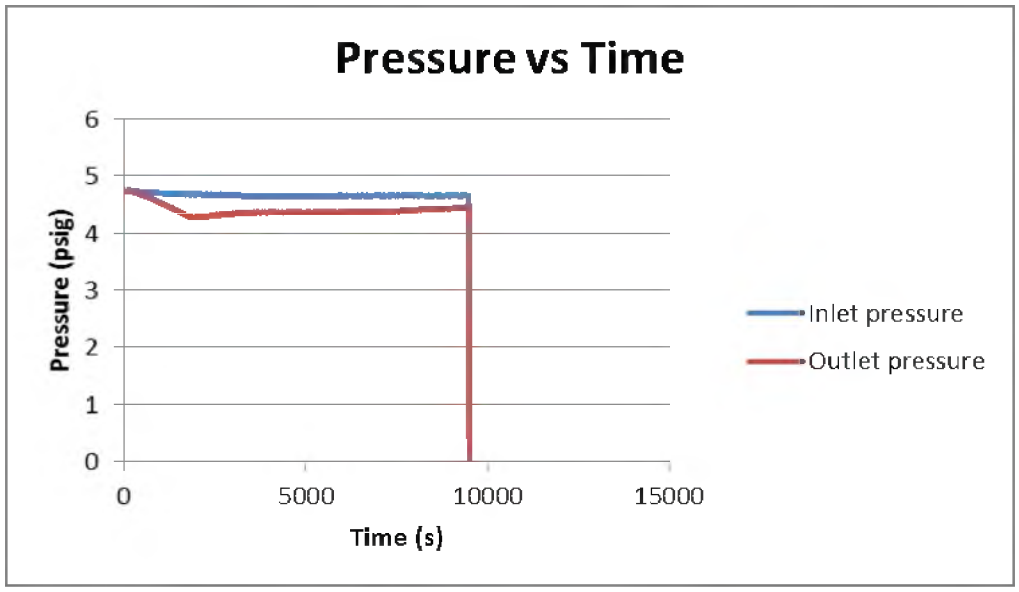

Figure A.18. Run number 3. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 10 °C (0.3 °C per minute).

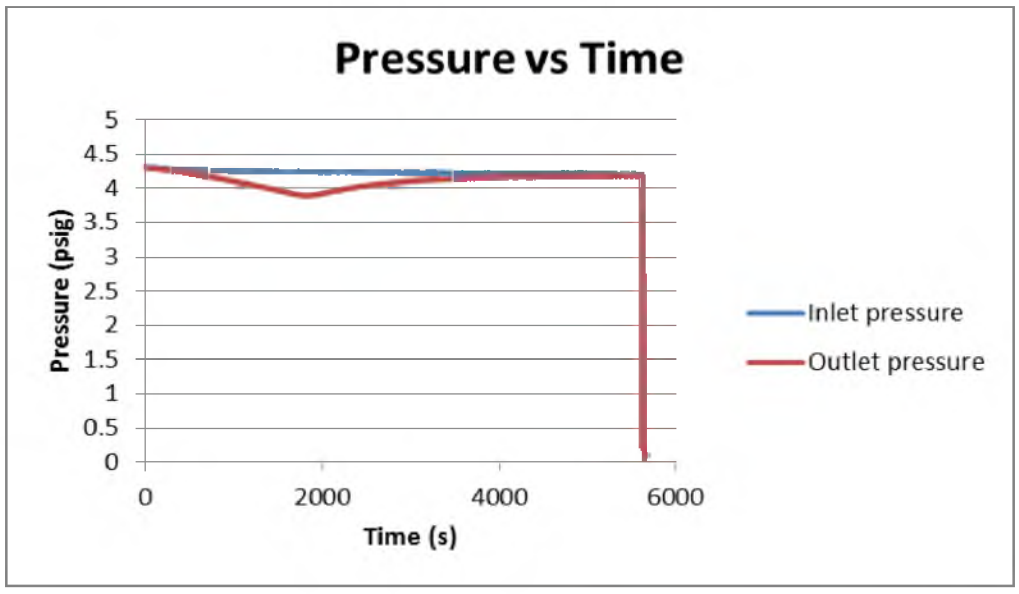

Figure A.19. Run number 4. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 10 °C (0.3 °C per minute).

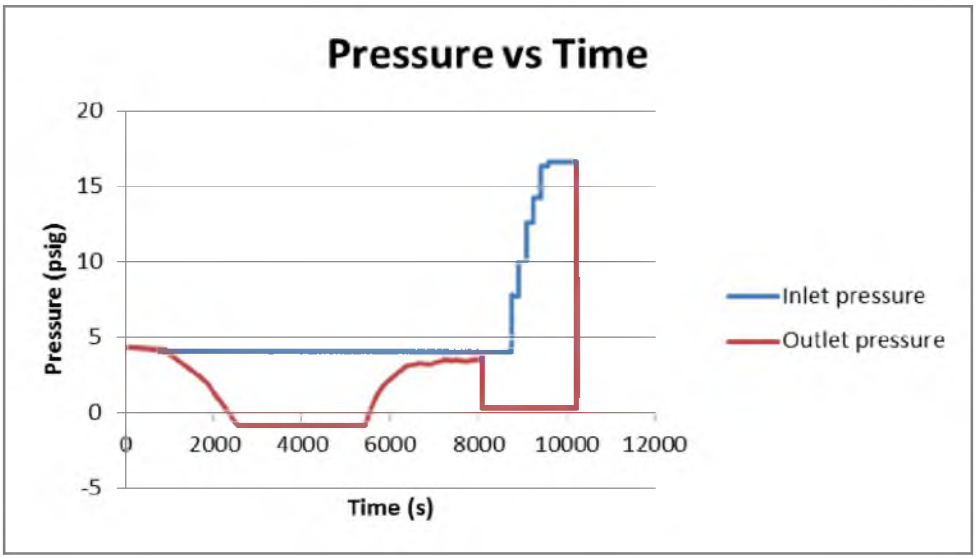

Figure A.20. Applied an upstream pressure of 4 psig with a slurry condition at WAT and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36 and 40.5 psig (measured by manually observing a pressure gauge).

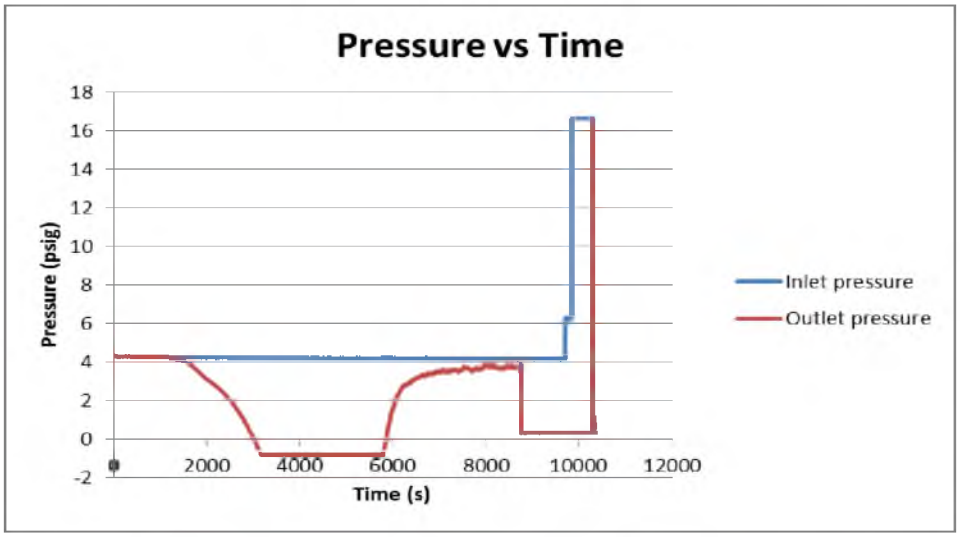

Figure A.21. Applied an upstream pressure of 4 psig with a slurry condition at 30 and cooled down to 5 °C (0.3 °C per minute). *The gel broke between 36 and 40.5 psig (measured by manually observing a pressure gauge).

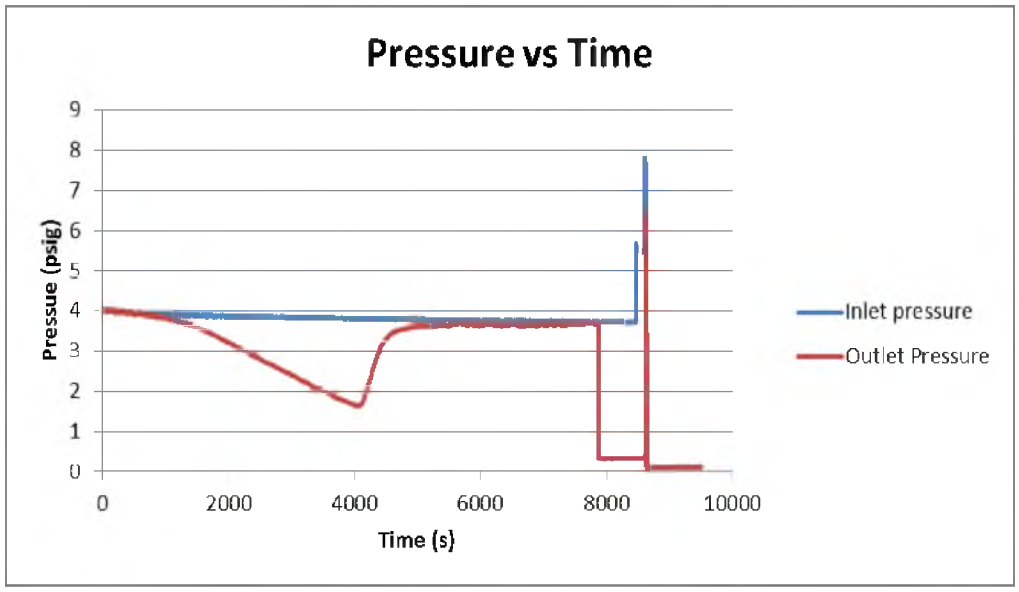

Figure A.22. Run number 1. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 5 °C (0.3 °C per minute).

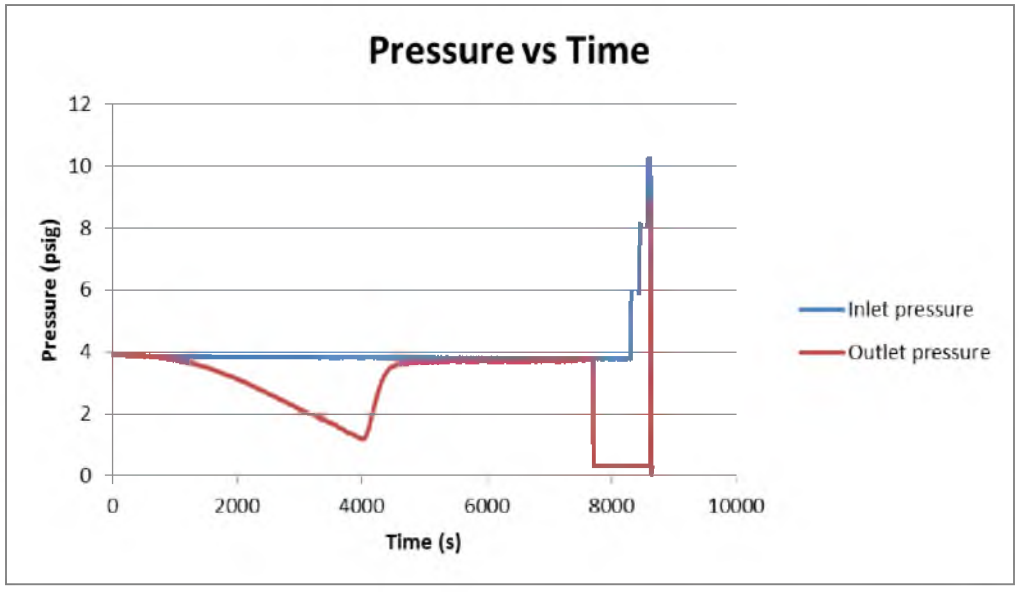

Figure A.23. Run number 3. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 5 °C (0.3 °C per minute).

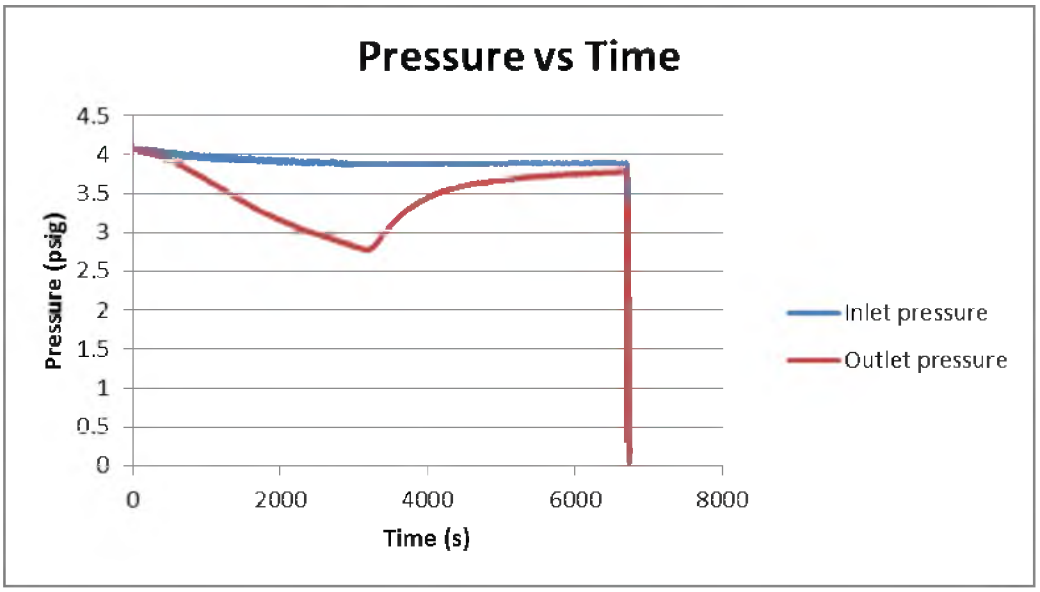

Figure A.24. Run number 1. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 5 °C (0.3 °C per minute).

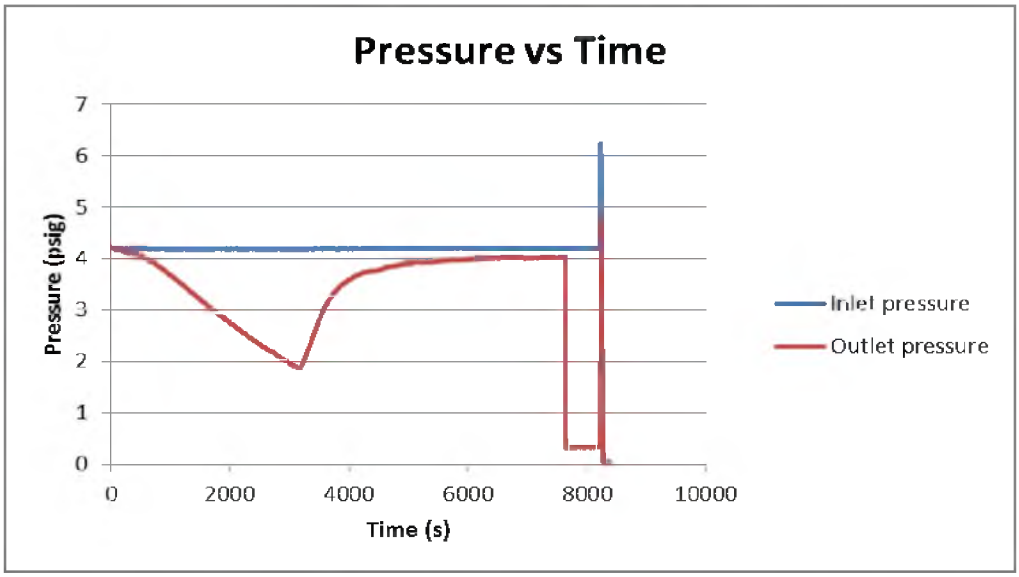

Figure A.25. Run number 2. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 5 °C (0.3 °C per minute).

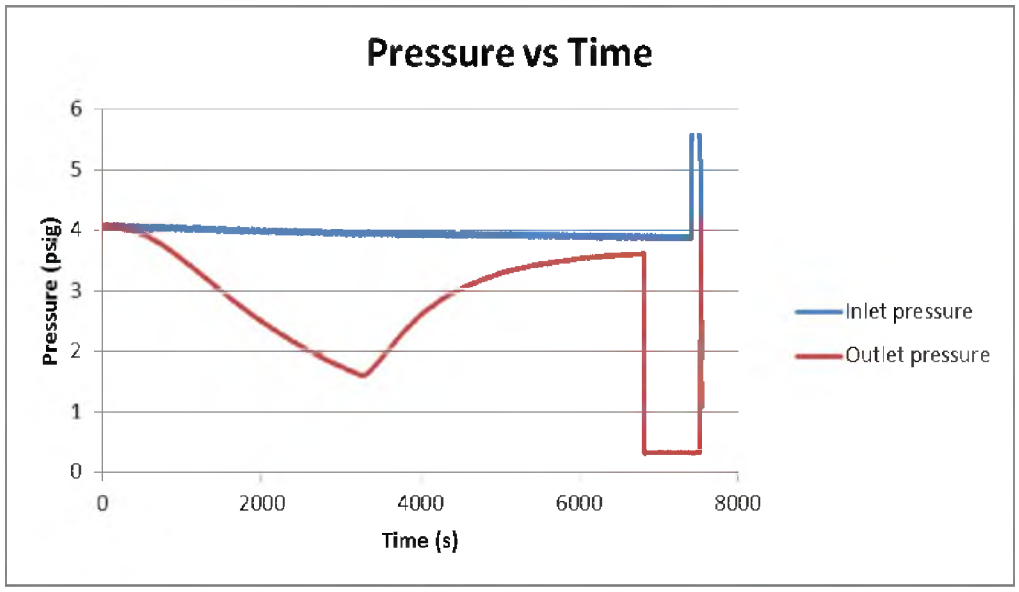

Figure A.26. Run number 3. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 5 °C (0.3 °C per minute).

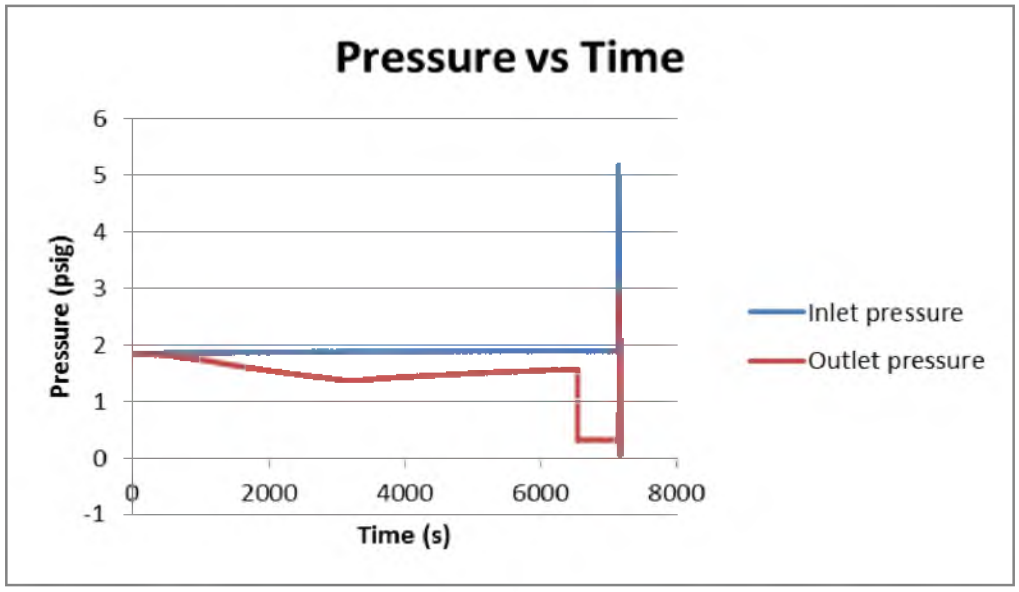

Figure A.27. Run number 5. Applied an upstream pressure of 2 psig with a slurry condition at 20 °C and cooled down to 5 °C (0.3 °C per minute).

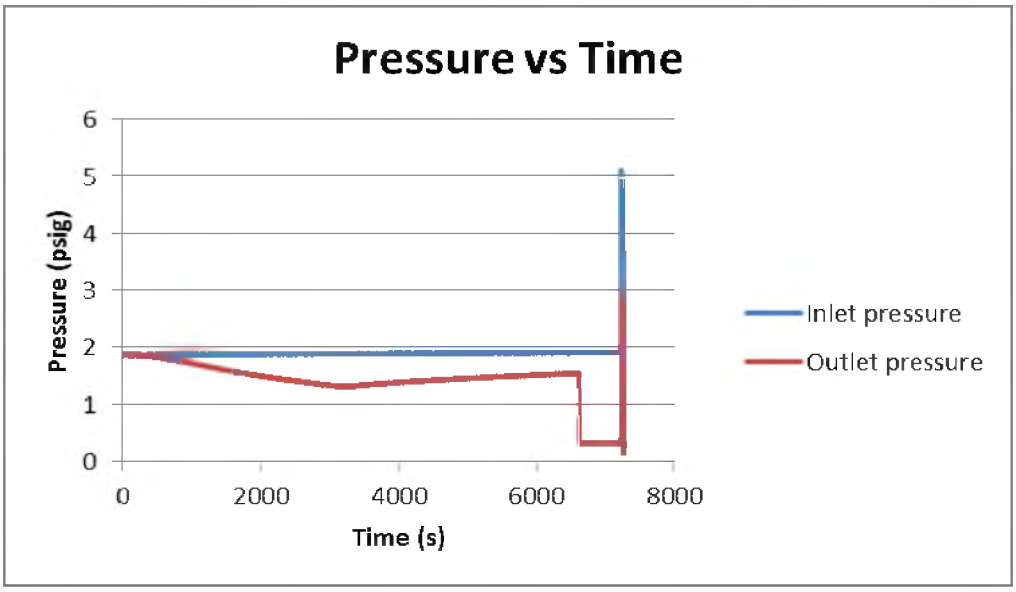

Figure A.28. Run number 6. Applied an upstream pressure of 2 psig with a slurry condition at 20 °C and cooled down to 5 °C (0.3 °C per minute).

A12. Slurry restart condition, 15-5 °C, 0.3 °C per min

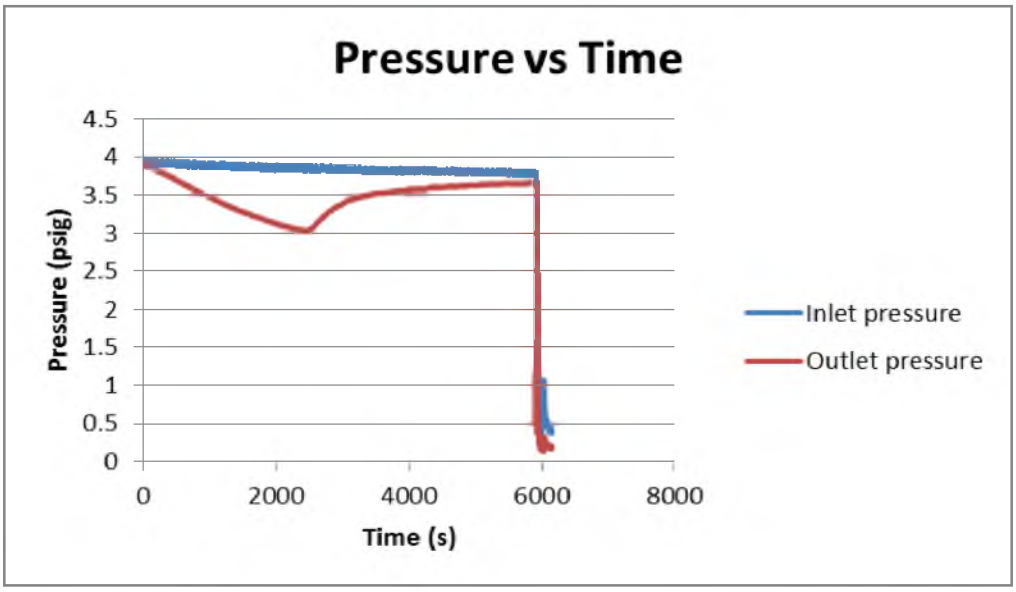

Figure A.29. Run number 1. Applied an upstream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 5 °C (0.3 °C per minute).

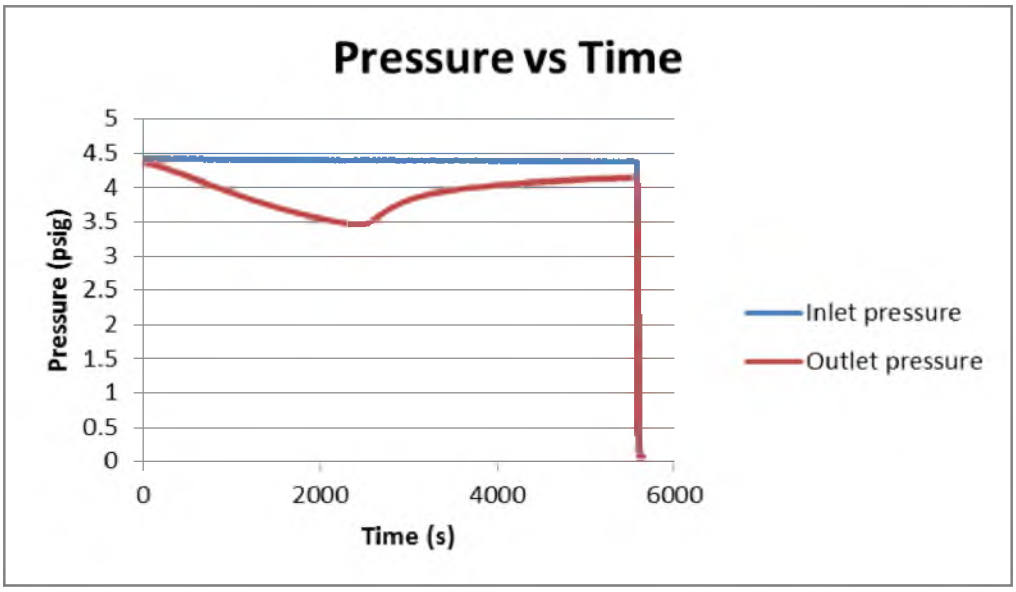

Figure A.30. Run number 2. Applied an upstream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 5 °C (0.3 °C per minute).

A13. Slurry restart, condition 25-0 °C, 0.3 °C per min

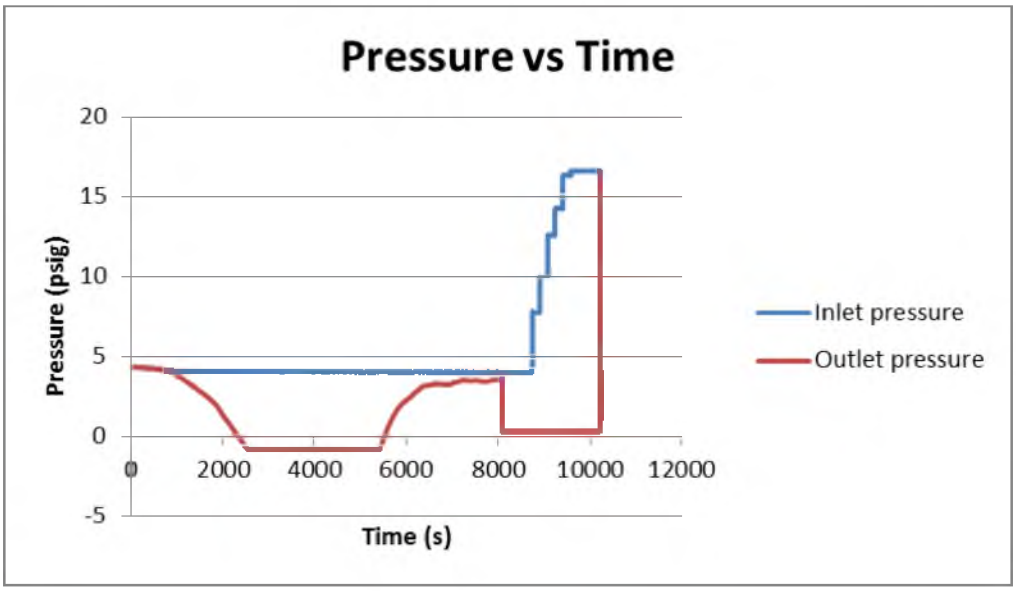

Figure A.31. Run number 2. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 0 °C (0.3 °C per minute). *The gel broke between 16.6 and 20.1 psig (measured by manually observing a pressure gauge).

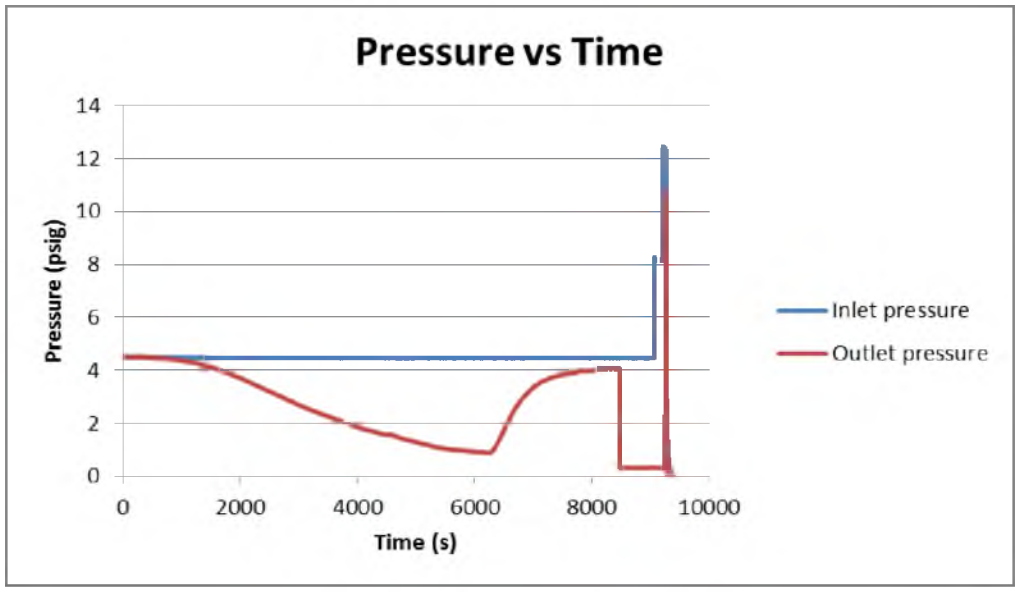

Figure A.32. Run number 3. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 0 °C (0.3 °C per minute).

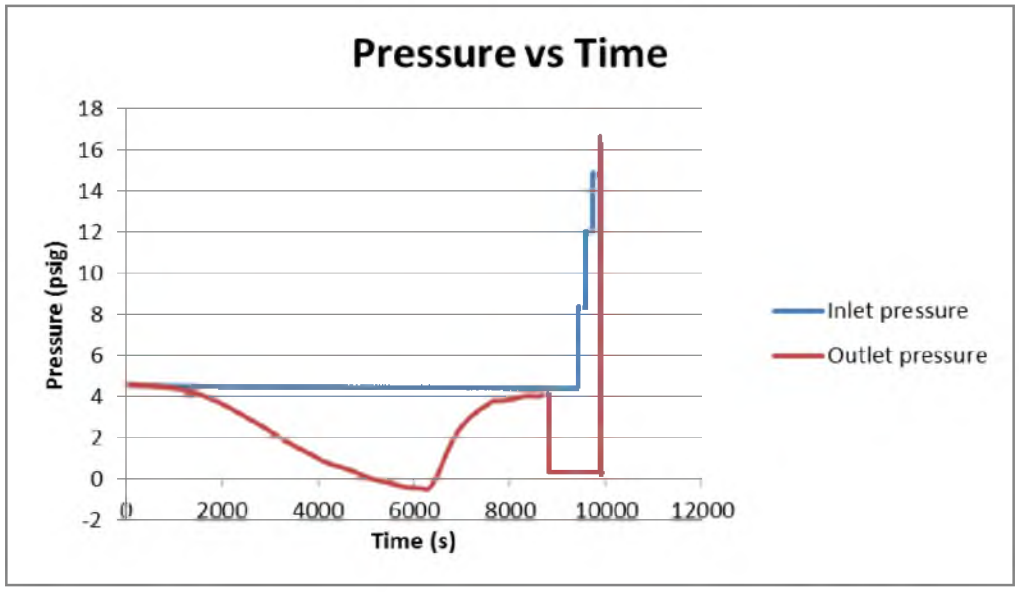

Figure A.33. Run number 4. Applied an upstream pressure of 4 psig with a slurry condition at 25 °C and cooled down to 0 °C (0.3 °C per minute). *The gel broke between 14.8 and 20.1 psig (measured by manually observing a pressure gauge)

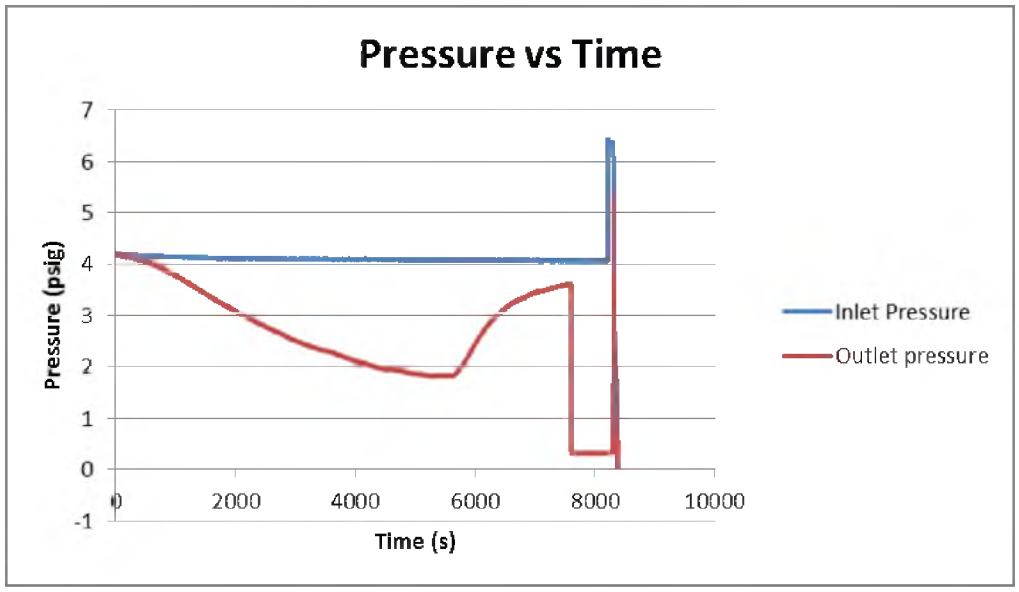

Figure A.34. Run number 1. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 0 °C (0.3 °C per minute).

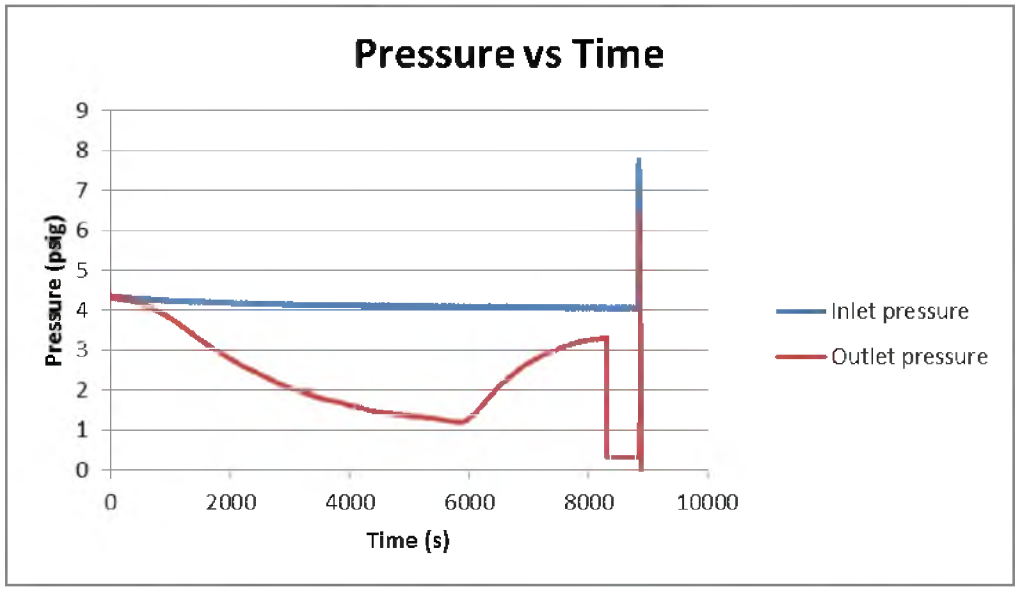

Figure A.35. Run number 2. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 0 °C (0.3 °C per minute).

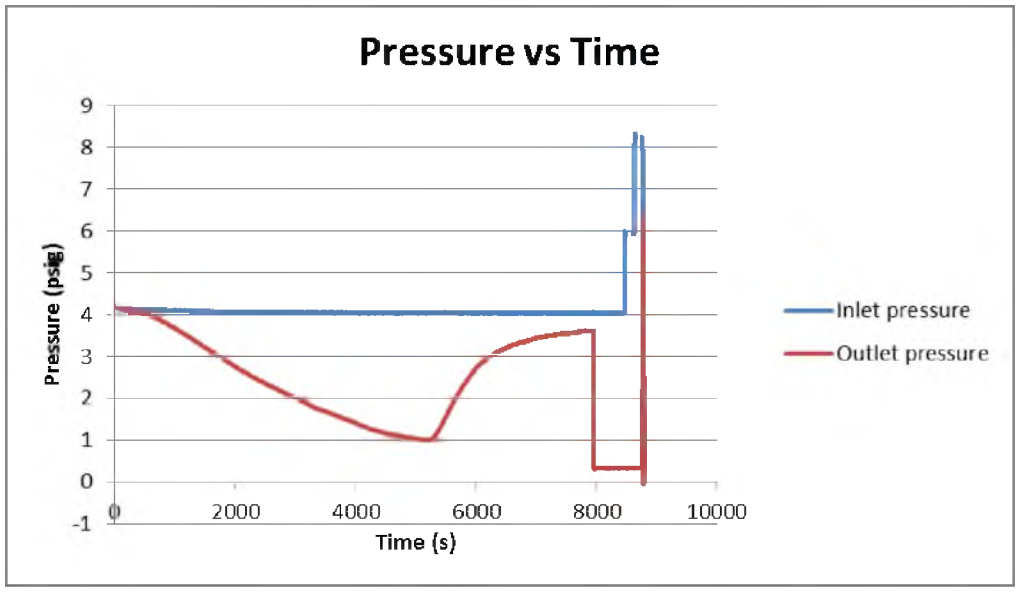

Figure A.36. Run number 3. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 0 °C (0.3 °C per minute).

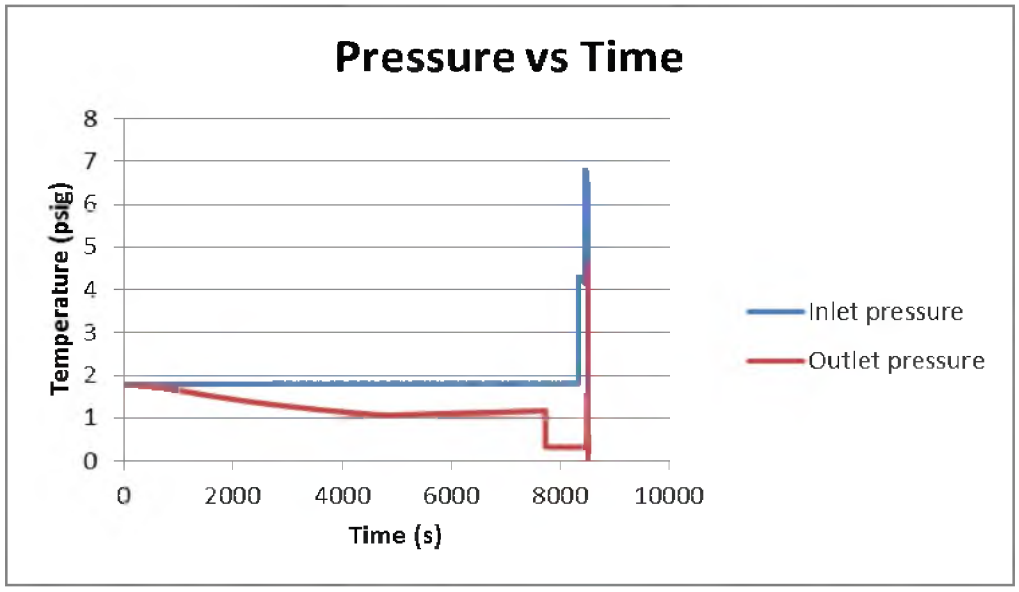

Figure A.37. Run number 4. Applied an upstream pressure of 4 psig with a slurry condition at 20 °C and cooled down to 0 °C (0.3 °C per minute).

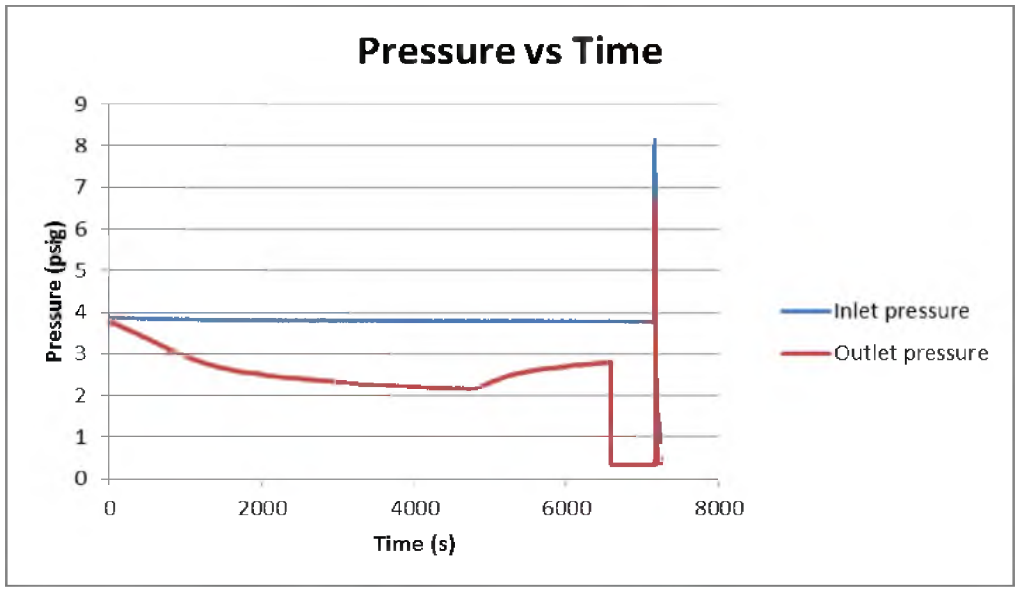

Figure A.38. Run number 1. Applied an upstream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 0 °C (0.3 °C per minute).

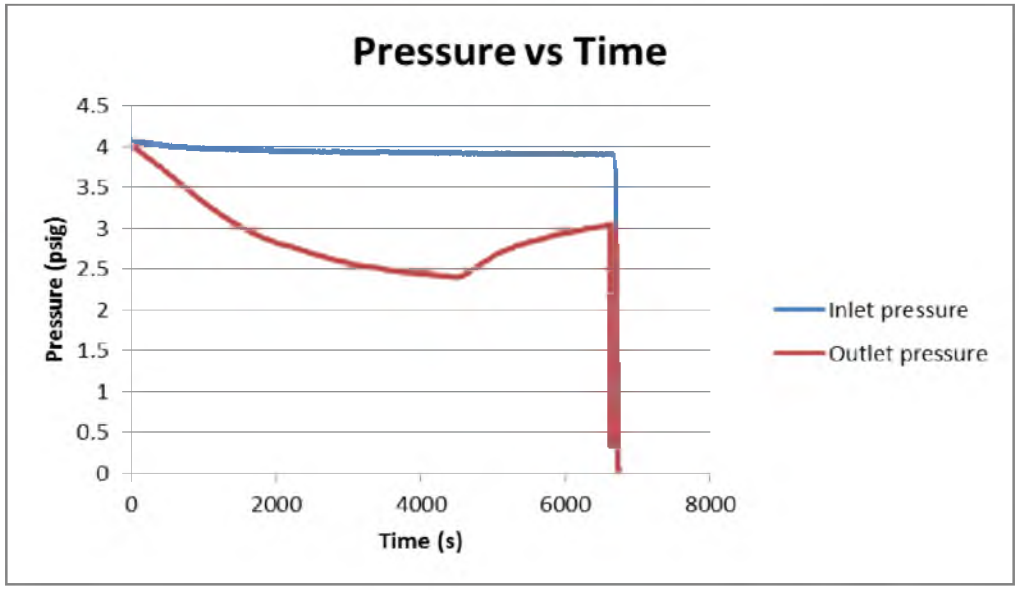

Figure A.39. Run number 2. Applied an up stream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 0 °C (0.3 °C per minute).

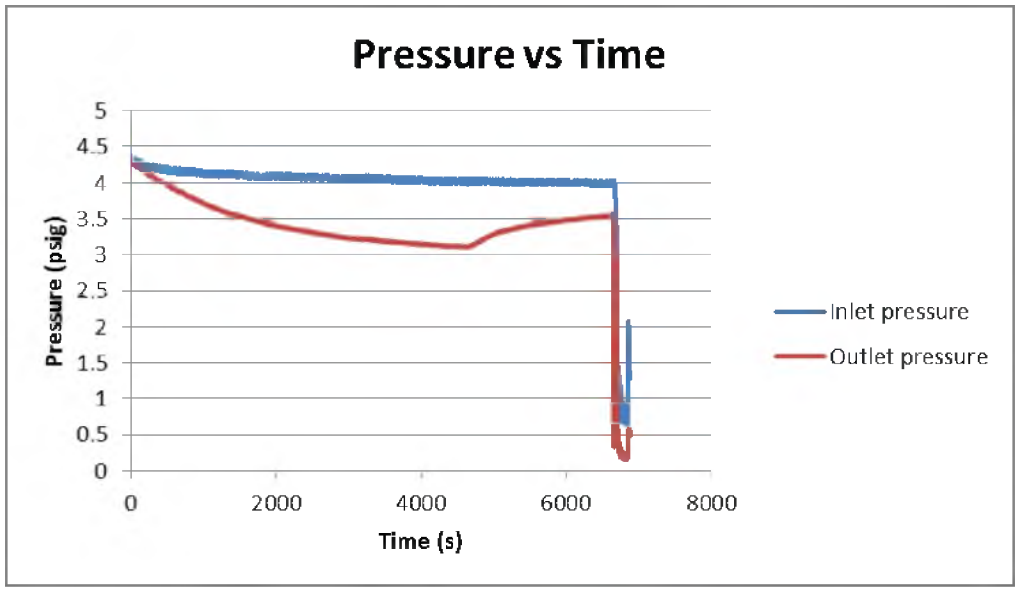

Figure A.40. Run number 3. Applied an up stream pressure of 4 psig with a slurry condition at 15 °C and cooled down to 0 °C (0.3 °C per minute).

A16. Rheometer raw data

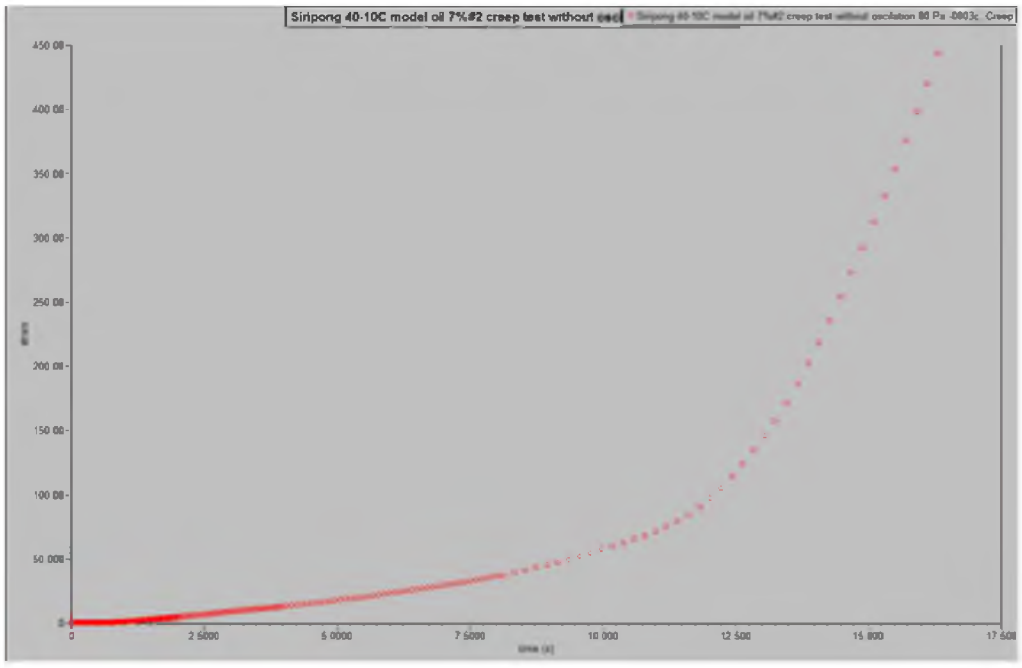

Figure A.41. Run number 2. Creep test at 80 Pa. Condition: 40-10 °C, 0.3 °C per minute.

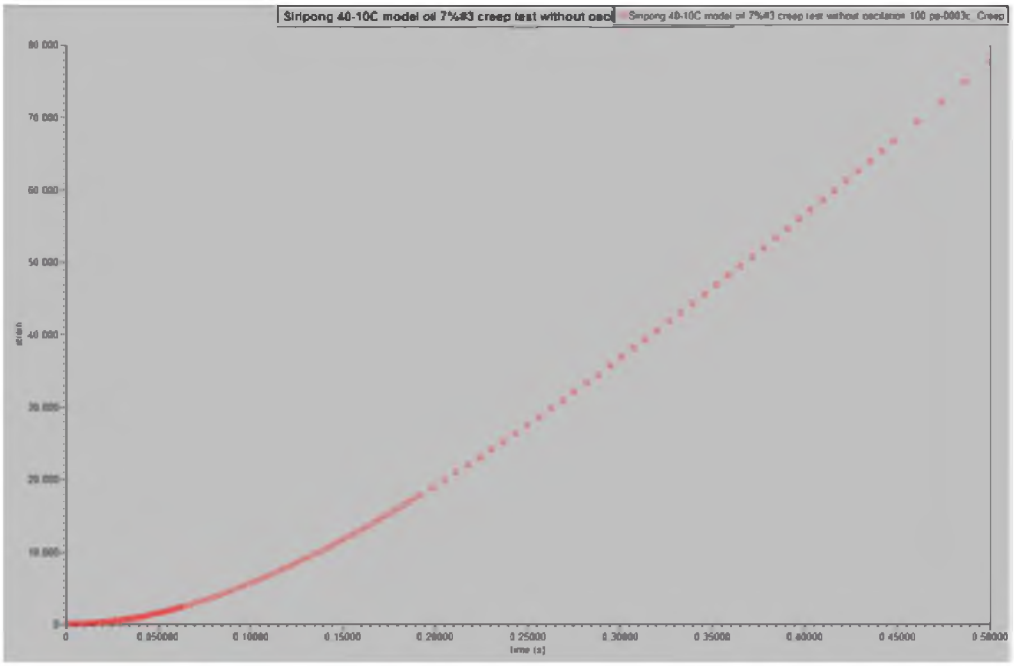

Figure A.42. Run number 3. Creep test at 80 Pa. Condition: 40-10 °C, 0.3 °C per minute.

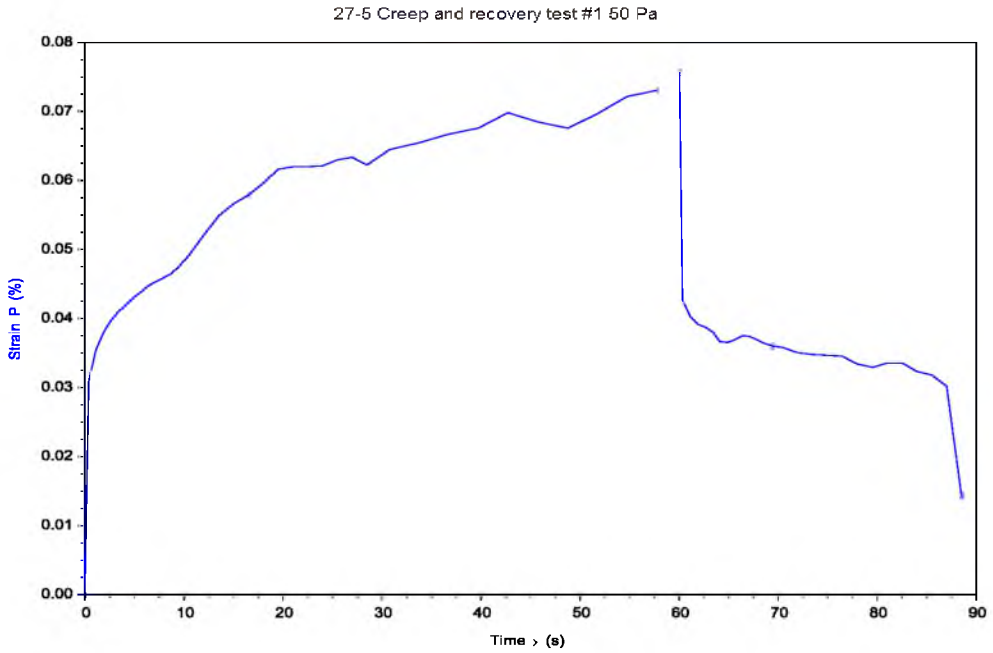

Figure A.43. Run number 1. Creep and recovery test at 50 Pa. Slurry from 27-5 °C, and 0.3 °C per minute.

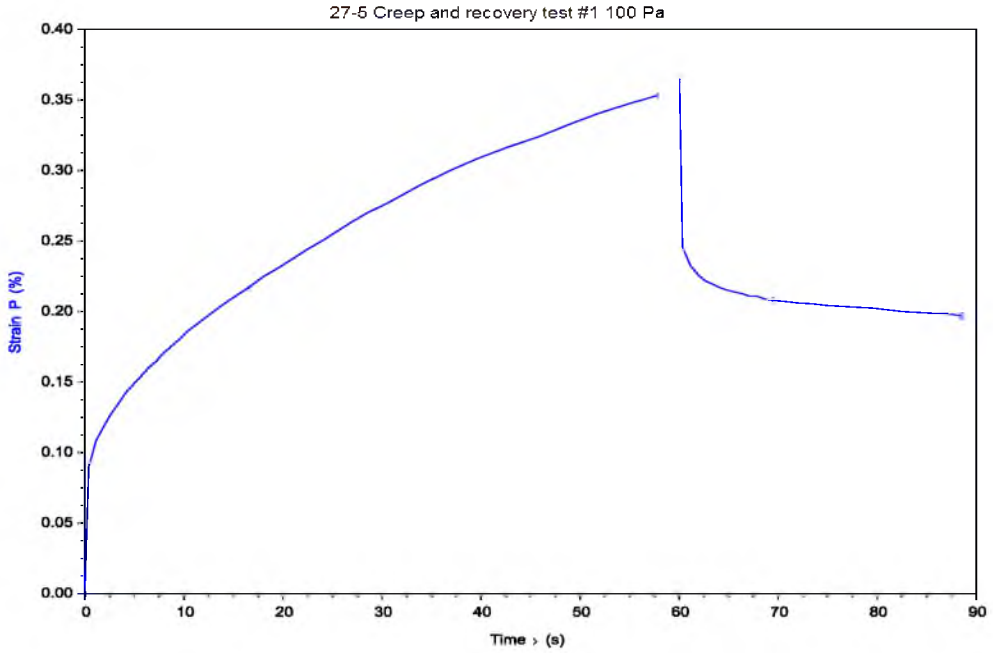

Figure A.44. Run number 1. Creep and recovery test at 100 Pa. Slurry from 27-5 °C, and 0.3 °C per minute.

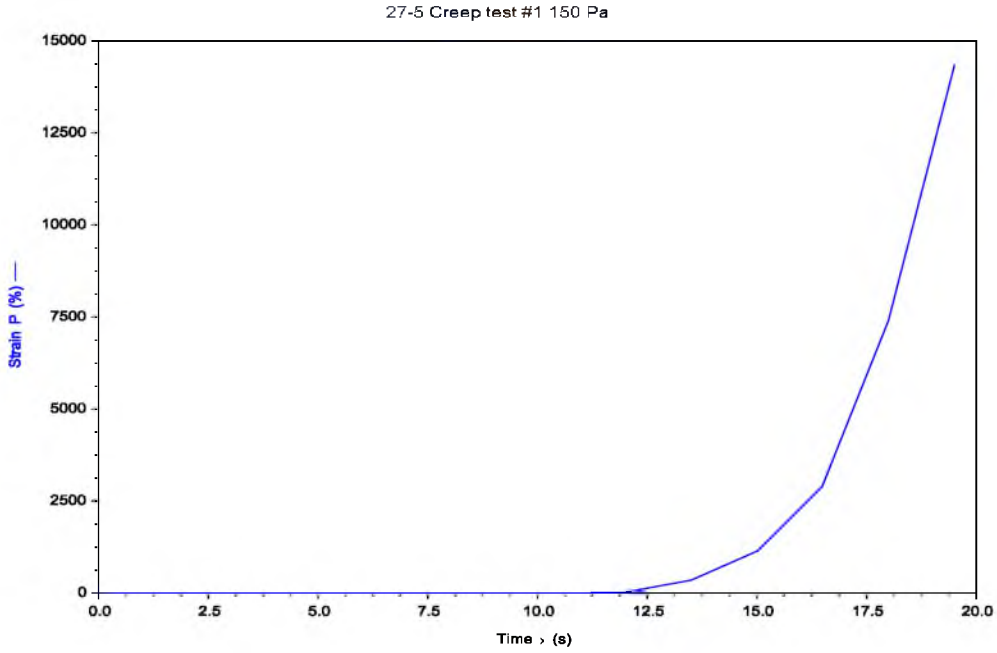

Figure A.45. Run number 1. Creep test at 150 Pa. Slurry from 27-5 °C, and 0.3 °C per minute.

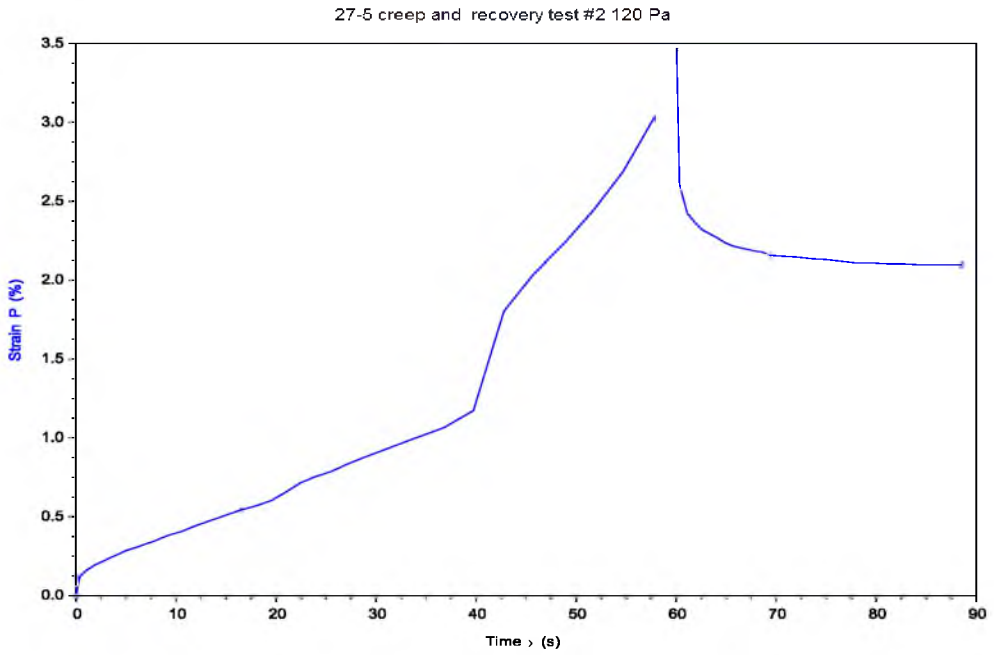

Figure A.46. Run number 2. Creep and recovery test at 120 Pa. Slurry from 27-5 °C, and 0.3 °C per minute.

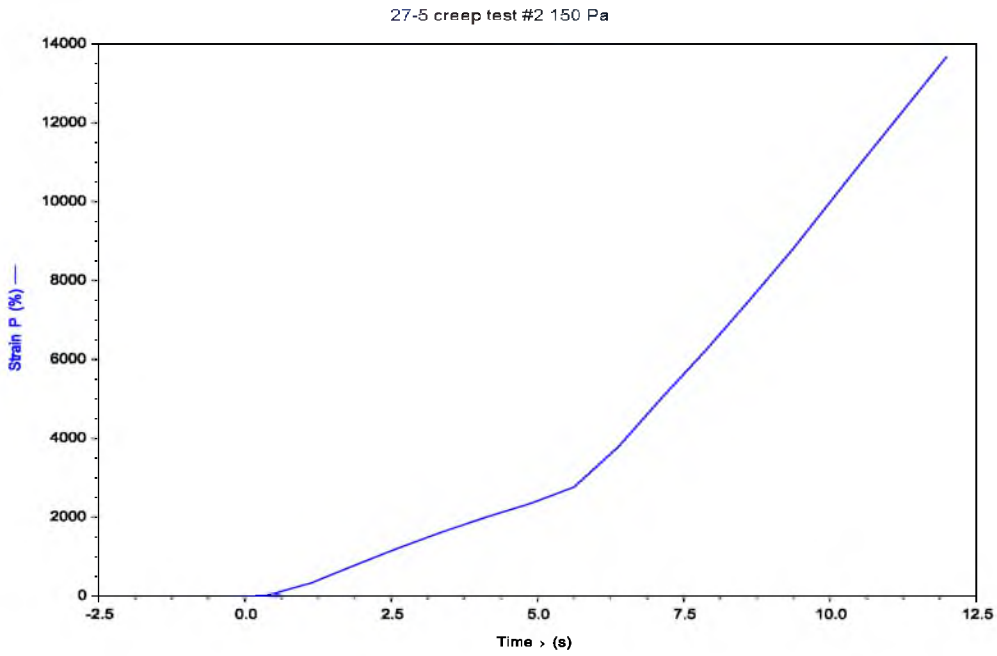

Figure A.47. Run number 2. Creep test at 150 Pa. Slurry from 27-5 °C, and 0.3 °C per minute.

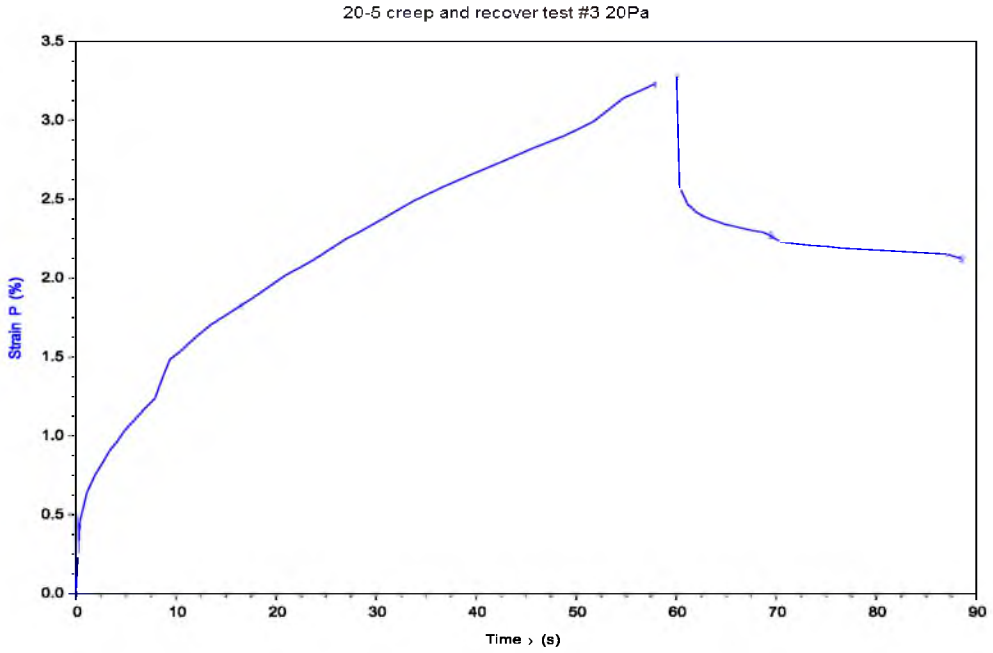

Figure A.48. Run number 3. Creep and recovery test at 20 Pa. Slurry from 25-5 °C, and 0.3 °C per minute.

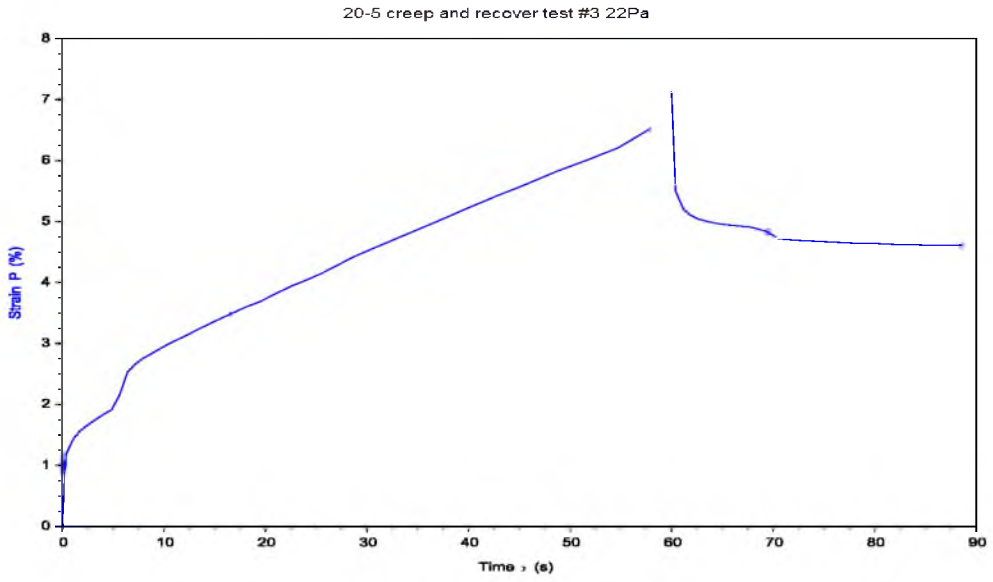

Figure A.49. Run number 3. Creep and recovery test at 22 Pa. Slurry from 25-5 °C, and 0.3 °C per minute.

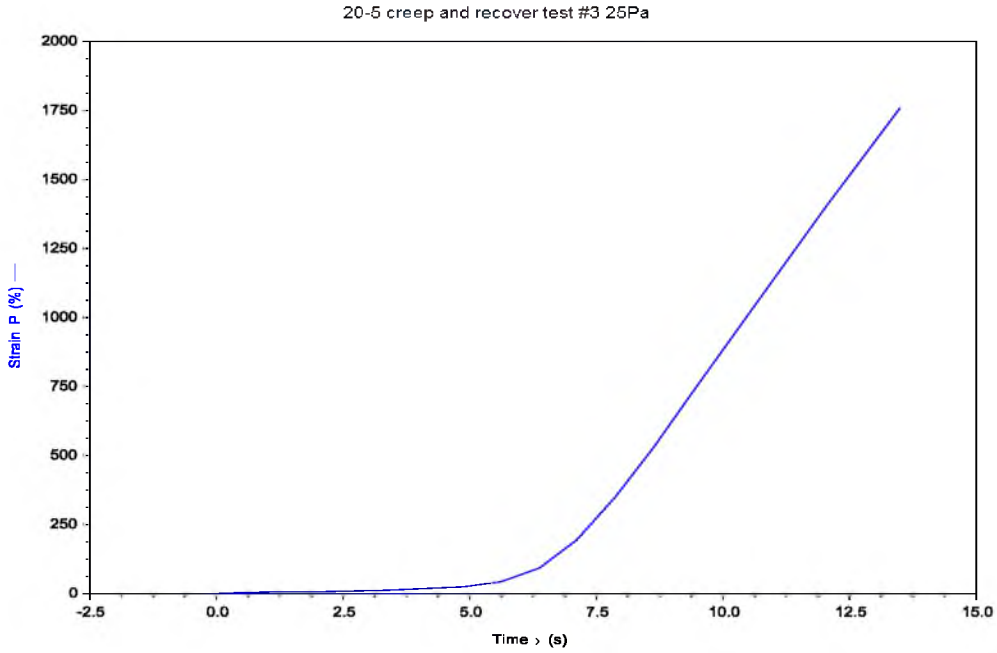

Figure A.50. Run number 3. Creep test at 25 Pa. Slurry from 25-5 °C, and 0.3 °C per minute.

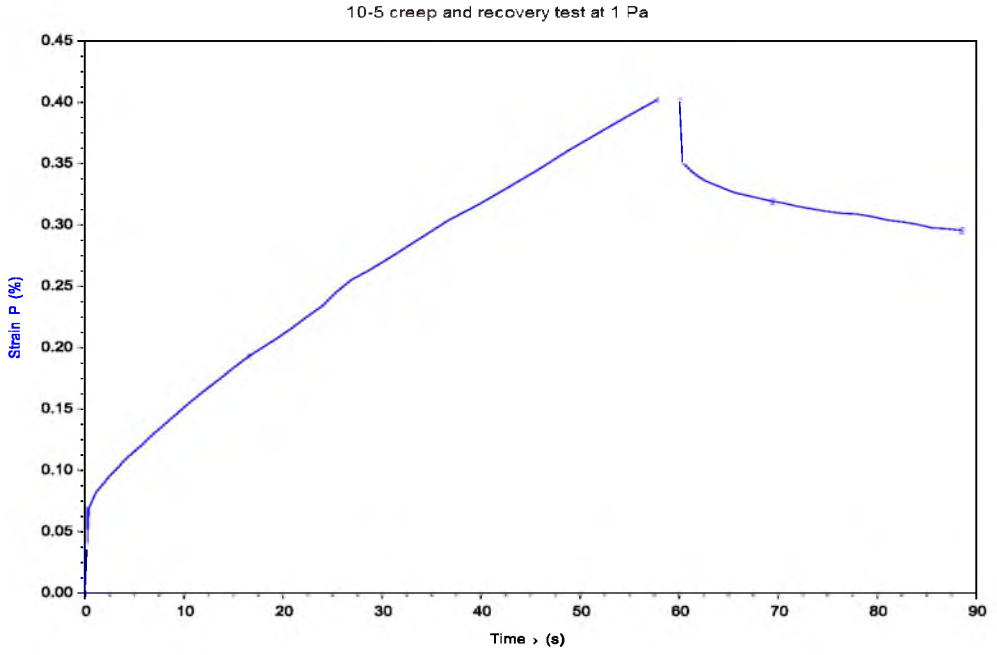

Figure A.51. Run number 2. Creep and recovery test at 1 Pa. Slurry from 10-5 °C, and 0.3 °C per minute.

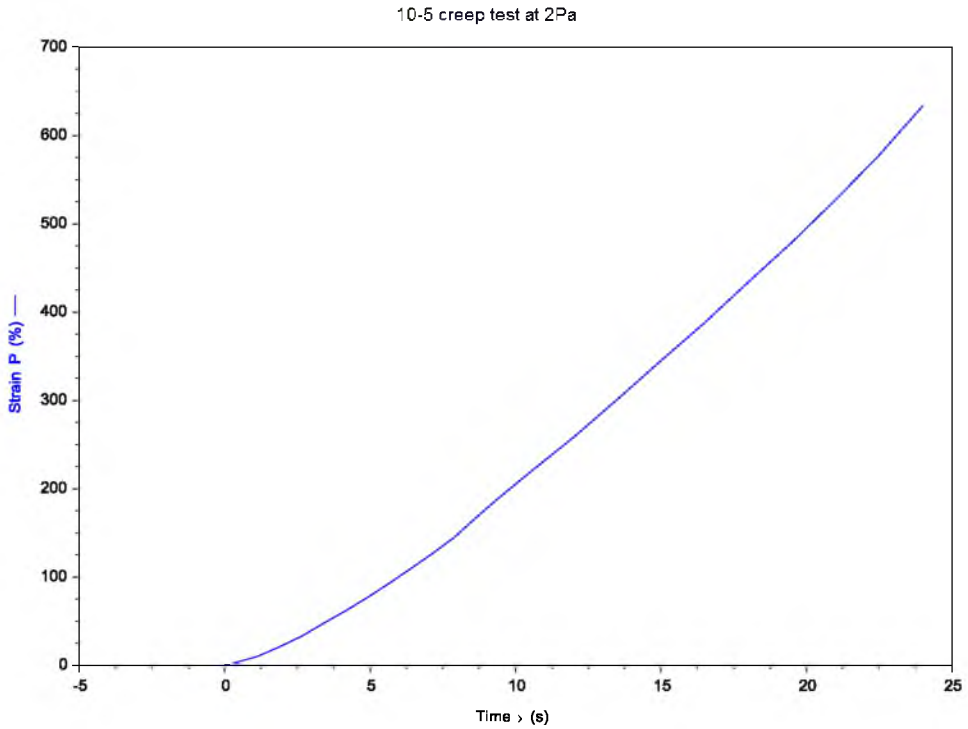

Figure A.52. Run number 2. Creep test at 2 Pa. Slurry from 10-5 °C, and 0.3 °C per minute.

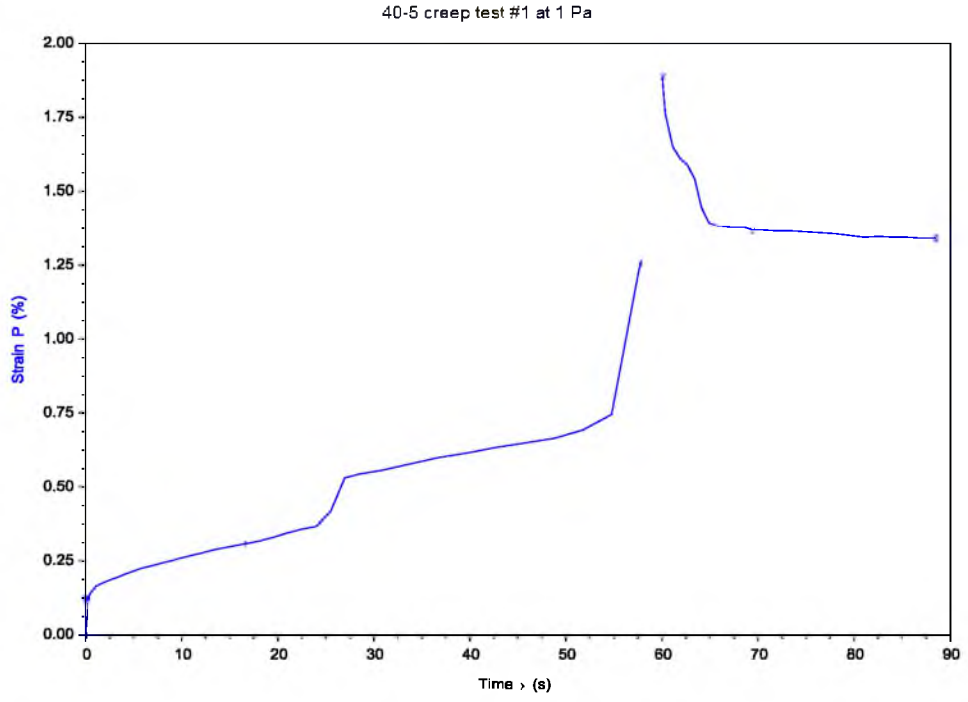

Figure A.53. Run number 1. Creep and recovery test at 1 Pa. Slurry at constant 5 °C after imposing shear rate until gel reaches a temperature of 5 °C.

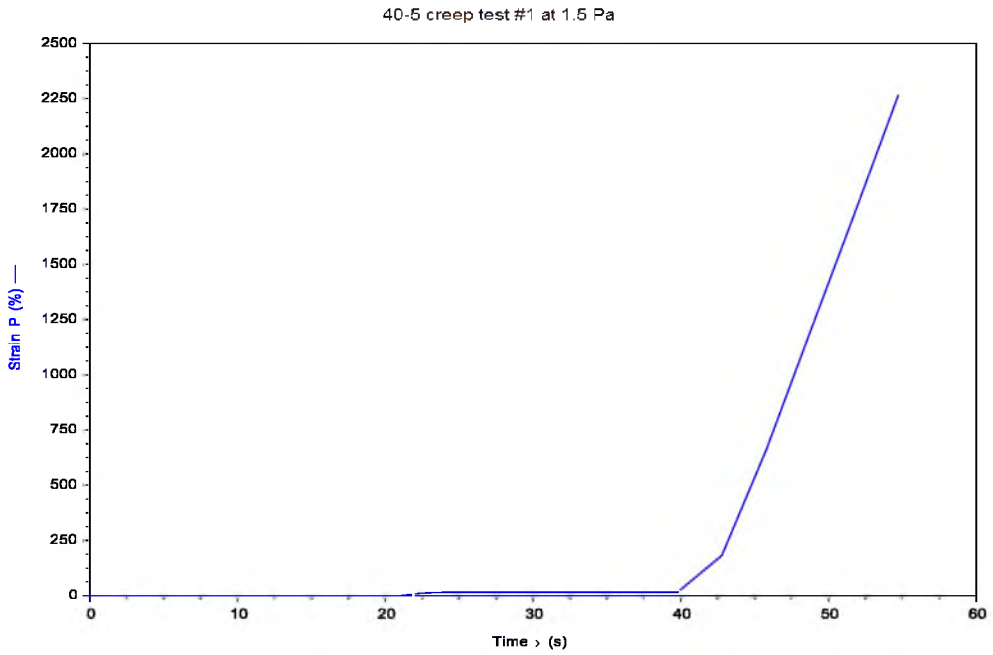

Figure A.54. Run number 1. Creep and recovery test at 1.5 Pa. Slurry at constant 5 °C after imposing shear rate until gel reaches a temperature of 5 °C.

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